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Syntheses of Peptides Related to the N-Terminal Structure of Corticotropin. I. Synthesis of Ser-Tyr-Ser-Met Sequence

By Ken INOUYE and Hideo OTSUKA

(Received May 31, 1960)

The hypophyseal polypeptide hormones, the corticotropin and melanocyte-stimulating hormone (MSH), have a common amino acid sequence within their structures[1,2].

By Harris and Lerner[1,3] it has been shown that hog α-MSH is an *N*-acetyltridecapeptide amide and its amino acid sequence, Ser-Tyr-Ser-Met-Glu-His-Phe-Arg-Try-Gly-Lys-Pro-Val, is identical with that occurring in the first tridecapeptide portion of corticotropin. This evidence affords a chemical basis for the intrinsic MSH activity[4,5] of corticotropin.

Considerably large fragments can be enzymatically or chemically removed from the carboxyl end of the molecule of corticotropin without loss of its biological activity[6]. While it has been reported that periodate oxidation of the *N*-terminal serine of corticotropin[7] or the cleavage of peptide bonds in the *N*-terminal Ser-Tyr-Ser segment of the molecule[6] results in complete depression of its ACTH activity, at the same time significant increase in the melanocyte expanding activity is observed[7].

The further detailed relationship between the two biological activities and the chemical structure must await the synthetic studies of active polypeptides.

Synthesis of *N*-terminal twenty sequence of corticotropin was done by Boissonnas et al. and the product exhibited a positive though limited ACTH activity[8]. Guttmann and Boissonnas[9] have recently synthesized the complete structure of α-MSH and the synthetic hormone has been shown to possess the same properties as those of the natural hog α-MSH. Hofmann et al. have reported that the blocked tridecapeptide amide, Cbz-Ser-Tyr-Ser-Met-Glu(NH_2)-His-Phe-Arg-Try-Gly-(ε-Tos)-Lys-Pro-Val-NH_2, has 0.8×10^5 MSH units per gram[10] and the replacement of the carbobenzoxy group with an acetyl group results in some twenty-five fold increase in its activity[11]. The substituted polypeptide sequence of β-MSH has also been synthesized by Schwyzer et al.[12]

Here we wish to write concerning a part of our studies of synthetic peptides corresponding to the amino acid sequence common to corticotropin and α-MSH. The synthesis of Ser-Tyr-Ser-Met sequence will be described.

In the syntheses of serine-containing peptides we used *O*-benzylserine[13,14] as a starting material in place of serine to avoid unexpected side reactions which may be caused by the presence of the free hydroxyl group of the latter.

Carbobenzoxy-*O*-benzylseryltyrosine and -*O*-benzylserylmethionine methyl esters were obtained in good yields as compared with the corresponding serylpeptide derivatives[15,16], though as for the method of coupling, the anhydride procedure was different from the procedures used by the others.

The advantageous effect of *O*-benzylserine is much more remarkable in saponification of the peptide esters with alkali. It has been reported that the saponification of carbobenzoxyseryltyrosine methyl[16] or ethyl[15] ester gave only a 50 per cent yield of the desired product and the yield of carbobenzoxyserylmethionine was also significantly low (67%)[15]. However, we could derive carbobenzoxy-*O*-benzylseryltyrosine and -*O*-benzylserylmethionine and formyl-*O*-benzylserylmethionine in very high yields (near 90%) from the preceding methyl esters. The peptide bonds adjacent to the serine residues in corticotropin are sensitive to any alkali treatment[6] and Guttmann and

1) J. I. Harris and A. B. Lerner, *Nature*, **179**, 1346 (1957).
2) J. I. Harris, ibid., **184**, 167 (1959).
3) J. I. Harris, *Biochem. J.*, **71**, 451 (1959).
4) P. H. Bell, *J. Am. Chem. Soc.*, **76**, 5565 (1954); **78**, 5051 (1956).
5) H. B. F. Dixon, *Biochim. Biophys. Acta*, **19**, 392 (1956).
6) R. G. Shepherd, S. D. Willson, K. S. Howard, P. H. Bell, D. S. Davies, S. B. Davis, E. A. Eigner and N. E. Shakespeare, *J. Am. Chem. Soc.*, **78**, 5067 (1956).
7) H. B. F. Dixon, *Biochem. J.*, **62**, 25p (1956).
8) R. A. Boissonnas, St. Guttmann, J.-P. Waller and P.-A. Jaquenoud, *Experientia*, **12**, 446 (1956).
9) St. Guttmann and R. A. Boissonnas, *Helv. Chim. Acta*, **42**, 1257 (1959).
10) K. Hofmann, M. E. Woolner, H. Yajima, G. Spühler, T. A. Thompson and E. T. Schwartz, *J. Am. Chem. Soc.*, **80**, 6458 (1958).
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12) R. Schwyzer, H. Kappeler, B. Iselin, W. Rittel and H. Zuber, *Helv. Chim. Acta*, **42**, 1702 (1959).
13) K. Okawa and H. Tani, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 1199 (1954).
14) K. Okawa, This Bulletin, **29**, 486 (1956).
15) K. Hofmann, A. Jöhl, A. E. Furlenmeier and H. Kappeler, *J. Am. Chem. Soc.*, **79**, 1636 (1957).
16) St. Guttmann and R. A. Boissonnas, *Helv. Chim. Acta*, **41**, 1852 (1958).

Boissonnas[16] have, moreover, shown the fact that the saponification of serine peptide esters is accompanied by the cleavage of peptide bond at the carboxyl side of serine residue. However, we could not observe such a fact in regard to the *O*-benzylserine peptides.

On removal of carbobenzoxy and *O*-benzyl groups from carbobenzoxy-*O*-benzylserylmethionine methyl ester by hydrobromic acid/acetic acid or catalytic hydrogenation we failed to obtain the desired dipeptide ester, presumably because of the instability of the thioether bond. Sheehan and Yang[17] have shown that a formyl group, which is easily removed by mild acid solvolysis, can be used on peptide syntheses as an amino protecting function in conjugation with the carbodiimide procedure without racemization of the products. Following this procedure, formyl-*O*-benzylserine and methionine methyl ester were coupled with *N, N'*-dicyclohexylcarbodiimide (DCCI) to give formyl-*O*-benzylserylmethionine methyl ester which could be deformylated to *O*-benzylserylmethionine methyl ester without any difficulties.

Coupling of carbobenzoxy-*O*-benzylseryltyrosine with *O*-benzylserylmethionine methyl ester by DCCI yielded almost quantitatively the acyltetrapeptide ester, carbobenzoxy-*O*-benzylseryltyrosyl-*O*-benzylserylmethionine methyl ester in crystalline form.

Experimental

All amino acids used are of L-configuration. The melting point was determined in a capillary tube in a sulfuric acid bath and not corrected.

***O*-Benzylserine Methyl Ester Hydrochloride.**—To 20 ml. of anhydrous methanol previously cooled below −10°C, was added dropwise 1.33 ml. (0.0184 mol.) of thionylchloride and then 3 g. (0.0154 mol.) of *O*-benzylserine was introduced[13,14]. The mixture was stirred for 1.5 hr. at room temperature and then allowed to stand overnight. The resulting clear solution was evaporated under reduced pressure. The residue was crystallized from acetone-ether to give 3.44 g. (91%). Recrystallization from methanol-ether yielded needles, m. p. 141.5~142°C with decomposition.

Found: N, 5.86; Cl, 14.41. Calcd. for $C_{11}H_{16}O_3$·NCl: N, 5.69; Cl, 14.43%.

***N*-Formyl-*O*-benzylserine.**—This was prepared after the usual procedure for optically active formylamino acids of Sheehan and Yang[17]. 1.95 g. of *O*-benzylserine was formylated and the product was recrystallized from water to give 1.77 g., m. p. 137.5~138.5°C, $[\alpha]_D^{25}=+52.9\pm1°$ (*c* 2.613 in ethanol).

Found: C, 59.31; H, 6.03; N, 6.39. Calcd. for $C_{11}H_{13}O_4N$: C, 59.3; H, 5.88; N, 6.29%.

***N*-Carbobenzoxy-*O*-benzylseryltyrosine Methyl Ester.**—To a solution of 8.23 g. (0.025 mol.) of *N*-carbobenzoxy-*O*-benzylserine[15] (m. p. 100.5~101°C, $[\alpha]_D^{25}=+12.0\pm2°$ (*c* 2.448 in acetic acid)) in 75 ml. of tetrahydrofuran/dioxane (1:4) were added 6.56 ml. (0.0275 mol.) of tri-*n*-butylamine and 2.63 ml. (0.0275 mol.) of ethylchloroformate at −5°C. After 15 min. a solution of tyrosine methyl ester (prepared from 6.37 g. (0.0275 mol.) of the hydrochloride[19] and 4.23 ml. (0.030 mol.) of triethylamine) in 8 ml. water and 32 ml. dioxane was introduced. The reaction mixture was stirred at room temperature for 4 hr. and evaporated under reduced pressure. The residue dissolved in 150 ml. of ethyl acetate was successively washed with 1N hydrochloric acid, water, 5% sodium bicarbonate and water and dried over sodium sulfate. The solution was evaporated to a syrupy residue which was crystallized from methanol-ethyl acetate-petroleum ether, 12.3 g. (97.2%), m.p. 108~111.5°C. Recrystallization from ethyl acetate-petroleum ether yielded 10.2 g. (80.6%), m. p. 112~114.5°C, $[\alpha]_D^{25}=+14.6\pm2°$ (*c* 3.068 in 99% ethanol). (lit.[15] m. p. 111~112°C, $[\alpha]_D^{25}=+15.5°$ (*c* 2.84 in 99% ethanol).

Found: C, 66.32; H, 6.13; N, 5.41. Calcd. for $C_{29}H_{30}O_7N_2$: C, 66.3; H, 5.97; N, 5.53%.

***N*-Carbobenzoxy-*O*-benzylseryltyrosine.**—2.533 g. (0.005 mol.) of *N*-carbobenzoxy-*O*-benzylseryltyrosine methyl ester was saponified in 12.5 ml. of methanol with 5.0 ml. (0.01 mol.) of 2N Sodium hydroxide at room temperature for one hour, yielding 2.34 g. (95.0%). Recrystallization from ethyl acetate-petroleum ether gave 2.20 g. (89.5%), m. p. 158.5~159.5°C, $[\alpha]_D^{25}=+39.4\pm1°$ (*c* 2.086 in ethanol).

Found: C, 65.38; H, 5.88; N, 5.72. Calcd. for $C_{28}H_{28}O_7N_2$: C, 65.6; H, 5.74; N, 5.70%.

***N*-Carbobenzoxy-*O*-benzylserylmethionine Methyl Ester.**—4.12 g. (0.0125 mol.) of *N*-carbobenzoxy-*O*-benzylserine and methionine methyl ester (prepared from 2.80 g. (0.014 mol.) of the hydrochloride) were coupled in a tetrahydrofuran/dioxane solution almost exactly as in the case of *N*-carbobenzoxy-*O*-benzylseryltyrosine methyl ester. Yield 5.1 g. (86%), m. p. 69.0~70.5°C. Recrystallization for analysis from ethyl acetate-petroleum ether gave a sample with m. p. 69.5~71°C.

Found: C, 60.56; H, 6.48; N, 5.76. Calcd. for $C_{24}H_{30}O_6N_2S$: C, 60.8; H, 6.38; N, 5.91%.

***N*-Carbobenzoxy-*O*-benzylserylmethionine.**—3.56 g. (0.0075 mol.) of *N*-carbobenzoxy-*O*-benzylserylmethionine methyl ester was saponified in 18 ml. of methanol with 4.2 ml. of 2N sodium hydroxide at room temperature for 30 min. The product was recrystallized from ethyl acetate-ether to yield 3.17 g. (92%), m. p. 152~152.5°C.

Found: N, 5.95; S, 7.00. Calcd. for $C_{23}H_{28}O_6N_2S$: N, 6.09; S, 6.97%.

***N*-Formyl-*O*-benzylserylmethionine Methyl Ester.**—To a suspension of 6.59 g. (0.033 mol.) of methionine methyl ester hydrochloride in 50 ml. of ether was added 20 ml. of ice-cold 50% potassium carbonate. The mixture was shaken at 0°C until the solid disappeared. The ether layer which separated was dried over sodium sulfate at 0°C and concentrated

17) J. C. Sheehan and D. D. H. Yang, *J. Am. Chem. Soc.*, **80**, 1154 (1958).

18) K. Okawa, This Bulletin, **29**, 488 (1956).

19) R. A. Boissonnas, St. Guttmann, P. -A. Jaquenoud and J. -P. Waller, *Helv. Chim. Acta*, **38**, 1491 (1955).

in vacuo to an oil. This oily residue was dissolved in 50 ml. of methylene chloride and the solution was mixed with a suspension of 6.69 g. (0.03 mol.) of *N*-formyl-*O*-benzylserine in 50 ml. of methylene chloride. To the resulting clear solution was added at 0°C 6.20 g. (0.03 mol.) of dicyclohexylcarbodiimide dissolved in 15 ml. of methylene chloride. The reaction mixture was stirred at room temperature for 5 hr. and then refrigerated. The separated dicyclohexylurea was collected by filtration, yielding 6.45 g. (95.8%). The filtrate was cooled in ice, washed with ice-cold 1 N hydrochloric acid, ice-water, 5% sodium bicarbonate and finally with water and dried over sodium sulfate. The concentration of the solution gave a syrupy residue which was crystallized from tetrahydrofuran-ether to yield colored needles, 7.55 g., m. p. 73~76°C. An additional 1.0 g. of crystal was obtained from the mother liquor. Total yield, 8.55 g. (77.4%). These crops, reddish orange in color, were combined and dissolved in ethyl acetate and chromatographed on 125 g. of aluminum oxide. Elution with the same solvent gave colorless fractions which were combined and concentrated in vacuo. Crystallization of the resulting syrup from ethyl acetate ether yielded colorless and odorless needles, 7.025 g. (63.5%), m. p. 78.5~79.5°C, $[\alpha]_D^{25} = -23.2 \pm 1°$ (*c* 2.08 in methanol).

Found: C, 55.84; H, 6.84; N, 7.42; S, 8.69. Calcd. for $C_{17}H_{24}O_5N_2S$: C, 55.5; H, 6.57; N, 7.61; S, 8.70%.

***N*-Formyl-*O*-benzylserylmethionine.**—1.54 g. (0.0042 mol.) of *N*-formyl-*O*-benzylserylmethionine methyl ester was saponified in 11 ml. of dioxane with an equivalent amount of 1 N sodium hydroxide at room temperature for one hour. The resulting solution was diluted with ice-water to 30 ml. and neutralized with ice-cold 1 N hydrochloric acid to a separate crystalline precipitate, 1.30 g. (87.8%), m. p. 161~162°C. Recrystallization from ethanol-water gave 1.19 g. of needles, m. p. 163°C, $[\alpha]_D^{16} = -8.8 \pm 2°$ (*c* 2.095 in methanol).

Found: C, 54.49; H, 6.41; N, 7.96; S, 9.13. Calcd. for $C_{16}H_{22}O_5N_2S$: C, 54.20; H, 6.24; N, 7.88; S, 9.03%.

***O*-Benzylserylmethionine Methyl Ester.**—4.42 g. (0.012 mol.) of formyl-*O*-benzylserylmethionine methyl ester was dissolved in 40 ml. of *N*-methanolic hydrochloric acid and stored at room temperature overnight. After most of the methanol had been removed in vacuo the resulting colored syrup was dissolved in 40 ml. of water and washed several times with ethyl acetate. The colorless aqueous solution was concentrated in vacuo to a small volume and mixed with 15 ml. of 50% potassium carbonate and 40 ml. of ether at 0°C. The ether layer was separated and the alkaline phase was twice extracted with ether. The combined ether solution was dried over sodium sulfate at 0°C and concentrated to give a colorless and clear oil, 3.95 g. (97%). A sample was chromatographed on paper in the system of *n*-butanol-acetic acid-water (2 : 1 : 2) and only one spot positive to both ninhydrin and PtI_6^{2-} reagent[20] was detected.

***N*-Carbobenzoxy-*O*-benzylseryltyrosyl-*O*-benzylserylmethionine Methyl Ester.**—4.925 g. (0.01 mol.) of *N*-carbobenzoxy-*O*-benzylseryltyrosine and 3.95 g. of *O*-benzylserylmethionine methyl ester were dissolved in 80 ml. of methylene chloride. To this birefringent solution was added 2.063 g. (0.01 mol.) of dicyclohexylcarbodiimide in 20 ml. of methylene chloride at 0°C and the reaction mixture was stirred at room temperature. The birefringence of flow almost completely disappeared in about 10 min. as the crystalline dicyclohexylurea separated. After the stirring had been continued for 3 hr. the mixture was stored at room temperature overnight to turn into a semi-solid state. It was returned to a solution by gentle warming at the boiling point and the insoluble urea was filtered off. The filtrate was concentrated to dryness in vacuo and the resulting solid was recrystallized from ethyl acetate-ether to yield 8.03 g. (98.7%), m. p. 163~167°C. Repeated recrystallization from methylene chloride-ether afforded 7.00 g. (86%), m. p. 166~169°C. A sample for analyses was further recrystallized from methanol to needles, m. p. 171~173°C, $[\alpha]_D^{20} = -12.9 \pm 0.1°$ (*c* 1.986 in methanol), $[\alpha]_D^{25} = -16.1 \pm 1°$ (*c* 2.008 in dimethylformamide).

Found: C, 63.54; H, 6.34; N, 6.95; S, 3.87. Calcd. for $C_{43}H_{50}O_{10}N_4S$: C, 63.5; H, 6.19; N, 6.88; S, 3.84%.

Summary

1. Carbobenzoxy-*O*-benzylseryltyrosyl-*O*-benzylserylmethionine methyl ester, which has the *N*-terminal tetrapeptide sequence of corticotropin and α-MSH, has been synthesized.

2. It has been shown that the *O*-benzylseryl peptide bond is very stable to an alkali treatment.

3. Syntheses of the relating serine peptide derivatives have been described.

The authors are indebted to Mr. Makoto Kanayama for valuable technical assistance.

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20) R. J. Block, E. L. Durrum and G. Zweig, "A Manual of Paper Chromatography and Paper Electrophoresis", Academic Press Inc., Publishers, New York (1955), p. 94.

Syntheses of Peptides Related to the N-Terminal Structure of Corticotropin. II. Synthesis of Gly-Lys-Pro-Val Sequence

By Ken INOUYE and Hideo OTSUKA

(Received June 27, 1960)

The sequence, Gly-Lys-Pro-Val is found at positions 10 to 13 in corticotropin and α-MSH[1]. Boissonnas et al.[2,3] synthesized this sequence in the form of tritylglycyl-ε-carbobenzoxylysylprolylvaline methyl ester from the preceding intermediates, tritylglycyl-ε-carbobenzoxylysine (methyl ester) and (carbobenzoxy-)prolylvaline methyl ester, none of which have yet been obtained in any crystalline states.

In connection with our synthetic studies on the *N*-terminal structure of corticotropin we have now obtained this tetrapeptide sequence in another form, formylglycyl-ε-carbobenzoxylysylprolylvaline benzyl ester.

Formylglycine and ε-carbobenzoxylysine methyl ester were coupled in methylene chloride by the use of *N, N'*-dicyclohexylcarbodiimide to give formylglycyl-ε-carbobenzoxylysine methyl ester which was converted by saponification into formylglycyl-ε-carbobenzoxylysine. Both of these dipeptide derivatives were obtained in good yields and in crystalline states. When the coupling was done in dimethylformamide solution the yield of the desired product was less than 30 per cent and in addition a side product, formylglycyl-*N, N'*-dicyclohexylurea was isolated. The mixed acid anhydride procedure also notably lowered the yield and purity of the product.

Carbobenzoxypropoline was condensed with valine benzyl ester by the mixed anhydride method to carbobenzoxyprolylvaline benzyl ester which was easily crystallized. This was then decarbobenzoxylated with hydrogen bromide in glacial acetic acid and the resulting ester hydrobromide was treated with potassium carbonate to the free base.

Coupling of formylglycyl-ε-carbobenzoxylysine with prolylvaline benzyl ester by *N, N'*-dicyclohexylcarbodiimide yielded the tetrapeptide, formylglycyl-ε-carbobenzoxylysylprolylvaline benzyl ester as an amorphous solid. This product was negative to the ninhydrin test and after deformylation with *N*-methanolic hydrochloric acid gave only one spot on the paperchromatogram sprayed with ninhydrin. The complete acid hydrolysate was subjected to the quantitative amino acid analysis and was shown to be composed of glycine, lysine proline and valine in the molar ratio as expected.

1) See the References of the preceding paper of this work. This Bulletin, **34**, 1 (1961).

2) R. A. Boissonnas, St. Guttmann, J. -P. Waller and P. -A. Jaquenoud, *Experientia*, **12**, 446 (1956).

3) R. A. Boissonnas, St. Guttmann, R. L. Huguenin, P. -A. Jaquenoud and Ed. Sandrin, *Helv. Chim. Acta*, **41**, 1867 (1958).

Experimental

All amino acids used are of L-configuration. The melting point was determined in a capillary tube in a sulfuric acid bath and not corrected.

Formylglycine.—This was prepared after the usual procedure for DL-formylamino acids of Sheehan and Yang[4]. 3.75 g. of glycine was formylated and the product was recrystallized from water to give 4.20 g. (81.6%), m. p. 149°C with decomposition.

Found: C, 35.12; H, 4.99; N, 13.35. Calcd. for $C_3H_5O_3N$: C, 35.0; H, 4.89; N, 13.6%.

Formylglycyl-ε-carbobenzoxylysine Methyl Ester.—To a suspension of 9.10 g. (0.0275 mol.) of ε-carbobenzoxylysine methyl ester hydrochloride[5] in ether was added 23 ml. of ice-cold 50% potassium carbonate. The mixture was shaken and the organic layer separated was dried over sodium sulfate at 0°C. After removal of the solvent in vacuo the oily residue was dissolved in 115 ml. of methylene chloride and 2.58 g. (0.025 mol.) of formylglycine was added. As soon as most of the formylglycine had dissolved, 5.16 g. (0.025 mol.) of *N, N'*-dicyclohexylcarbodiimide in 25 ml. of methylene chloride was quickly added. The mixture was stirred for five hours and allowed to stand overnight at room temperature and refrigerated. The separated dicyclohexylurea was collected by filtration, yielding 5.45 g. (97.2%). The filtrate was cooled at 0°C, washed successively with ice-cold 1 N hydrochloric acid, water, 5% sodium bicarbonate and water and dried over sodium sulfate. Evaporation of the solvent in vacuo gave a clear syrup which was crystallized from methylene chloride-ether. Yield 8.93 g. (94.3%). This was recrystallized from ethyl acetate-ether to give 8.40 g. (88.7%), m. p. 76~78°C. $[\alpha]_D^{1}$ = −10.3±2° (*c* 2.901 in methanol).

Found: C, 57.02; H, 6.81; N, 10.89. Calcd. for $C_{15}H_{20}O_6N_2$: C, 57.1; H, 6.60; N, 11.0%.

When dimethylformamide was used as a solvent for this coupling reaction there was obtained, in

4) J. C. Sheehan and D-D. H. Yang, *J. Am. Chem. Soc.*, **80**, 1154 (1958).

5) M. Bergmann, L. Zervas and W. F. Ross, *J. Biol. Chem.*, **111**, 245 (1935).

addition to the desired peptide (in a 30% yield), a side product, formylglycyl-*N*,*N'*-dicyclohexylurea, m. p. 164.5~165.5°C.

Found: C, 62.46; H, 8.97; N, 13.69. Calcd. for $C_{16}H_{27}O_3N_3$: C, 62.2; H, 8.81; N, 13.6%.

Formylglycyl-ε-carbobenzoxylysine.—To a solution of 3.79 g. (0.01 mol.) of formylglycyl-ε-carbobenzoxylysine methyl ester in 27.5 ml. of dioxane was added 11 ml. of 1 N sodium hydroxide and the mixture was stirred at room temperature for one hour. After removal of a slight amount of insoluble precipitates the solution was diluted with water to about 80 ml., neutralized with 11 ml. of ice-cold 1 N hydrochloric acid and concentrated to about 25 ml. under reduced pressure. The concentrate was stored at 0°C overnight to complete the separation of crystals, 3.47 g. (95.1%). Recrystallization from water gave 3.28 g. (89.8%), m. p. 144~146°C, $[\alpha]_D^{24} = +13.1 \pm 0.2°$ (*c* 1.358 in methanol).

Found: C, 56.27; H, 6.33; N, 11.56. Calcd. for $C_{17}H_{23}O_6N_3$: C, 56.0; H, 6.35; N, 11.5%.

Carbobenzoxyproline[6]**.**—4.6 g. (0.04 mol.) of proline was carbobenzoxylated with 8 g. of benzylchloroformate in 30 ml. of 2 N sodium hydroxide at 0°C. When the reaction was over the solution was washed with ether to remove an excess of benzylchloroformate and acidified. The product was taken up into ethyl acetate and the extract was shaken with 5% sodium bicarbonate. The aqueous solution was acidified and reextracted with ethyl acetate. The organic extract was dried over sodium sulfate and concentrated in vacuo to a syrup which was crystallized from carbon tetrachloride-petroleum ether (1:2) to give 9.47 g. (95.3%), m. p. 75~78°C. Recrystallization from the same solvent afforded 9.30 g., m. p. 76~78°C, $[\alpha]_D^{29} = -57.7 \pm 2°$ (*c* 0.975 in glacial acetic acid) (in lit.[6], m. p. 76~77°C, $[\alpha]_D^{20} = -61.7°$ (*c* 5.3 in glacial acetic acid).

Found: C, 62.98; H, 6.05; N, 5.89. Calcd. for $C_{13}H_{15}O_4N$: C, 62.75; H, 6.08; N, 5.63%.

Valine Benzyl Ester Hydrochloride.—A mixture of 4 g. of valine and 10 g. of *p*-toluenesulfonic acid monohydrate in 40 ml. of benzyl alcohol was stirred on an oil bath at 100°C (internal temperature). To this solution were added 40 ml. portions of carbon tetrachloride at one hour intervals and distilled out from a side-arm. After 8 hr. the remaining carbon tetrachloride was completely removed under reduced pressure and the crude ester *p*-toluenesulfonate was precipitated with the addition of ether, 10.0 g., m. p. 157~159°C. 10.0 g. of the crystal obtained above was suspended in 150 ml. of ether and mixed with 40 ml. of ice-cold 50% potassium carbonate. The insoluble precipitate was filtered off and the ether layer was dried over sodium sulfate at 0°C. Dry hydrogen chloride gas was bubbled into this ether solution to separate the desired ester hydrochloride, 6.3 g., m. p. 137~139.5°C. Recrystallization from chloroform-ether afforded 6.1 g., m. p. 139~141°C, $[\alpha]_D^{29} = -12.7 \pm 4°$ (*c* 0.495 in 0.1 N hydrochloric acid).

Found: N, 5.76; Cl, 14.50. Calcd. for $C_{12}H_{15}O_2NCl$: N, 5.75; Cl, 14.60%.

6) A. Berger, J. Kurtz and E. Katchalski, *J. Am. Chem. Soc.*, 76, 5552 (1954).

Carbobenzoxyprolylvaline Benzyl Ester.—To a mixture of 2.49 g. (0.01 mol.) of carbobenzoxyproline and 2.39 ml. (0.01 mol.) of tri-*n*-butylamine in 10 ml. of tetrahydrofuran was added 0.96 ml. (0.01 mol.) of ethylchloroformate at −10°C. After 15 min. a solution of 2.44 g. (0.01 mol.) of valine benzyl ester hydrochloride and 2.39 ml. (0.01 mol.) of tri-*n*-butylamine in 10 ml. of tetrahydrofuran was introduced and the reaction mixture was then stirred at room temperature for 5 hr. and concentrated under reduced pressure. The syrupy residue was dissolved in 35 ml. of ethyl acetate, successively washed with 1 N hydrochloric acid, 15% sodium chloride, 5% sodium bicarbonate, and with 15% sodium chloride, and dried over sodium sulfate. The ethyl acetate solution was concentrated to about 10 ml. in vacuo and to this was added petroleum ether to separate an oily precipitate which was soon crystallized in needles, 4.0 g. (91.3%), m. p. 87~91°C. Recrystallization from the same solvent gave thin needles, m. p. 91~92°C, $[\alpha]_D^{29} = -78.6 \pm 1°$ (*c* 1.749 in methanol).

Found: C, 68.40; H, 6.96; N, 6.37. Calcd. for $C_{23}H_{30}O_5N_2$: C, 68.4; H, 6.90; N, 6.39%.

Prolylvaline Benzyl Ester.—2.63 g. (0.006 mol.) of carbobenzoxyprolylvaline benzyl ester was dissolved in 15 ml. of 21.2% (w/w) hydromromic acid/glacial acetic acid and the mixture was allowed to stand at room temperature for 50 min. at the end of which time about 80 ml. of anhydrous ether was added. The supernatant was decanted and an oily residue was dissolved in 10 ml. of water and washed twice with ether. A small aliquot of this aqueous solution was chromatographed on paper in the system of *n*-butanol-acetic acid-water (4:1:2) and there were detected two components which gave yellow spots with ninhydrin. The minor component with the lower R_f value is possibly due to prolylvaline, and it may be found that the benzyl ester is cleaved to some extent under the conditions used, but no other side reactions take place.

The aqueous solution of the crude ester hydrobromide was then concentrated to a small volume in vacuo and shaken with 20 ml. of ether and 10 ml. of 50% potassium carbonate at −10°C. The aqueous phase was extracted with additional ether. The combined ether extract was dried over sodium sulfate at 0°C and evaporated in vacuo to an oil, 1.47 g. which was directly used for the following coupling reaction.

Formylglycyl-ε-carbobenzoxylysylprolylvaline Benzyl Ester.—The prolylvaline benzyl ester obtained above was dissolved in 30 ml. of methylene chloride and 1.28 g. (0.0035 mol.) of formylglycyl-ε-carbobenzoxylysine was adedd. The mixture was stirred at 0°C to give a homogeneous but somewhat cloudy solution in 15 min. To this solution was then added 0.723 g. (0.0035 mol.) of *N*,*N'*-dicyclohexylcarbodiimide and the reaction mixture was stirred at room temperature for five hours and allowed to stand overnight at 4°C. Separated dicyclohexylurea was removed by filtration, 0.739 g. (94.3%) and the filtrate was concentrated in vacuo. A syrupy residue was dissolved in ethyl acetate and washed with ice-cold 1 N hydrochloric acid, water, 5% sodium bicarbonate and finally with water and

dried over sodium sulfate. Concentration of the ethyl acetate solution in vacuo gave a foamy residue which was dried over phosphorus pentoxide at room temperature in high vacuum to afford 2.22 g. (97.5%) as colorless powder, $[\alpha]_D^{18}=-62.2\pm0.1°$ (c 2.505 in methanol).

Found: C, 62.13; H, 7.43; N, 10.54. Calcd. for $C_{41}H_{45}O_8N_5$: C, 62.7; H, 6.97; N, 10.7%.

This product gave a negative ninhydrin test and after treatment with 1N methanolic hydrochloric acid for 16 hr. only one spot[7] was visible on a paper-chromatogram which was developed in *n*-butanol-acetic acid-water (4:1:2) and sprayed with ninhydrin.

A sample of the tetrapeptide derivative was hydrolyzed with 6N hydrochloric acid at 100°C for 20 hr. and the hydrolysate was subjected to quantitative amino acid analysis by the method of Levy[8]. It was found that the product had a composition of Gly/Lys/Pro/Val in a molar ratio of 1.0/1.1/0.9/1.1.

7) The color of this spot changed with time from yellow to purple. Such a phenomenon has often been observed in glycylpeptides (K. Narita, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 487 (1954)).

8) A. L. Levy, *Nature*, **174**, 126 (1954).

Summary

Formylglycyl-ε-carbobenzoxylysylprolylvaline benzyl ester, which has a sequence occurring in corticotropin and α-MSH, has been synthesized.

The authors are indebted to Mr. Makoto Kanayama for valuable technical assistance.

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Calculation on the Electronic States of the Acrolein Molecule by the Semi-Empirical Molecular Orbital Method

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(Received May 31, 1960)

It is known that the semi-empirical molecular orbital method proposed by Pariser and Parr[1] gives good agreement with observation for the $\pi-\pi^*$ transitions of conjugated hydrocarbons and heteromolecules. Anno et al.[2-4] used the Pariser-Parr method to calculate the electronic state energies of some molecules containing C=O and N atoms, obtaining reasonably good agreement between calculated and observed values. Eastwood and Snow[5] have carried out a detailed vibrational analysis for the $n-\pi^*$ absorption spectrum of acrolein, while the experiment in vacuum ultraviolet region was done by Walsh[6]. In a previous paper[7] we were not certain whether or not the very weak band at 24647 cm^{-1} in acrolein spectrum was due to a singlet-triplet transition. In order to get some information about the electronic state energies of the acrolein molecule, we calculated the electronic states of acrolein by the Pariser-Parr method which is expected also to yield successful results for the electronic state energies of some molecules exhibiting $n-\pi^*$ transitions.

1) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).
2) T. Anno, I. Matubara and A. Sadō, This Bulletin, **30**, 168 (1957).
3) T. Anno, I. Matubara and A. Sadō, *J. Chem. Phys.*, **26**, 967 (1957).
4) T. Anno and A. Sadō, ibid., **26**, 1759 (1957).
5) E. Eastwood and C. P. Snow, *Proc. Roy. Soc.*, **149A**, 446 (1935).
6) A. D. Walsh, *Trans. Faraday Soc.*, **41**, 498 (1945).
7) K. Inuzuka, This Bulletin, **33**, 678 (1960).

Calculation and Results

The calculation of the electronic state energies of acrolein was done with the semi-empirical method proposed by the previous authors[1-5]. The π-MO's take in this paper are

$$\phi_1=1/2(\chi_1^O+\chi_2^C+\chi_3^C+\chi_4^C)$$
$$\phi_2=1/2(\chi_1^O+\chi_2^C-\chi_3^C-\chi_4^C)$$
$$\phi_3=1/2(\chi_1^O-\chi_2^C-\chi_3^C+\chi_4^C)$$
$$\phi_4=1/2(\chi_1^O-\chi_2^C+\chi_3^C-\chi_4^C)$$

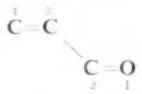
where χ_1^O, χ_2^C, χ_3^C and χ_4^C are $2p\pi$AO's of the oxygen and carbon atoms.

In addition to the above orbitals the acrolein molecule has a nonbonding orbital which can approximately be represented as follows:

$$\phi_n=\chi_n^O \qquad (5)$$

χ_n^O being the $2p\pi$AO of the oxygen atom, the nodal plane of which is perpendicular to the

molecular plane and contains the CO axis. The electron diffraction study of the acrolein molecule in the ground electronic state[8] shows that it is planar, having the following bond lengths and bond angles



$r_{12}=1.21\pm0.02$ Å
$r_{23}=1.46\pm0.03$ Å
$r_{31}=1.36\pm0.02$ Å
$\angle\gamma_{123}=\angle\gamma_{234}=120\pm3°$

Since the molecule belongs to the point group Cs, all the transition are symmetry-allowed. The energy integrals which appear in this calculation were evaluated according to the equation derived by Roothaan[9] and by Anno et al.[2] for the case of $r>2.80$ Å and of $r<2.80$ Å, respectively. We used Kon's formula[10] for the conculation of core integral β_{CO} between carbon and oxygen atoms, and the Pariser-Parr formula for β_{CC} between carbon and carbon atoms. For the evaluation of core integrals the Coulomb penetration integrals between next-neighboring neutral atoms were taken into consideration, and since we restricted the calculation of energy state up to 10 eV., singly and doubly excited electronic configurations[11] were taken in the calculation of energies for the excited electronic state. Since it is known that the calculation of energy state in $\pi-\pi^*$ transition usually results in a good agreement with the observed value without configuration interaction[12], we did not include the configuration interaction. On the other hand, as for $n-\pi^*$ transition the configuration interaction was taken into account but all the configurations more than 10 eV. higher than the ground configuration were neglected. Even for the configurations considered, we imposed the condition to reduce the order of the C.I. matrix: $(H_{ij}/H_{ii}-H_{jj})^2>1/10$, where H_{ij} is the interaction matrix element between the configurations i and j. Neglected configurations within the 10 eV. energy range were taken into account by the second order perturbation theory. Calculated energy values are shown in Table I. From this result it is seen that in acrolein the (n, π^*) triplet state is the lowest excited electronic state.

TABLE I. TRANSITION ENERGIES OF $n-\pi^*$ AND $\pi-\pi^*$ TRANSITIONS OF ACROLEIN MOLECULE

Orbital jump	Electronic transition	Transition energy no C.I. eV.	Transition energy including C.I. eV.	Experimental eV.
$n-\pi_3$	$^3A'\leftarrow{}^1A''$	5.55	2.85	
$n-\pi_3$	$^1A'\leftarrow{}^1A''$	5.98	3.85	3.71
$n-\pi_4$	$^3A'\leftarrow{}^1A''$	7.23	6.00	
$n-\pi_4$	$^1A'\leftarrow{}^1A''$	7.66	6.53	
$\pi_2, n-\pi_3, \pi_3$	$^3A'\leftarrow{}^1A''$	10.68	7.86	
$\pi_2, n-\pi_3, \pi_3$	$^1A'\leftarrow{}^1A''$	11.11	8.36	
$\pi_2-\pi_3$	$^3A'\leftarrow{}^1A'$	4.17		
$\pi_2-\pi_3$	$^1A'\leftarrow{}^1A'$	6.08		5.96
$\pi_2-\pi_4, \pi_1-\pi_3$	$^3A'\leftarrow{}^1A'$	5.85		
$\pi_2-\pi_4, \pi_2-\pi_3$	$^1A'\leftarrow{}^1A'$	7.76		
$\pi_1-\pi_4$	$^3A'\leftarrow{}^1A'$	7.53		
$\pi_1-\pi_4$	$^1A'\leftarrow{}^1A'$	9.44		

Discussion

Acrolein in *n*-hexane solution has three absorption maxima in the 1800~4000 Å region, λ's$_{max}$ 2078 Å (5.96 eV., $\log\varepsilon_{max}=3.89$), 3345 Å (3.71 eV., $\log\varepsilon_{max}=1.13$) and 4020 Å (3.08 eV., $\log\varepsilon_{max}=1.13$). The last two absorption bands are assigned to the $n-\pi^*$ transition from the solvent effect. The first absorption band has the extinction coefficient of 7700, showing that this transition may be regarded as an allowed one. It is assigned to a $\pi-\pi^*$ transition from the red-shift in the solvent effect.

From these observations the absorption bands at 5.96 and 3.71 eV., may be assigned to the $^1A'\leftarrow{}^1A'$ and $^1A'\leftarrow{}^1A''$ transitions, respectively. In Table I they correspond to the calculated 6.07 eV. (π, π^*) and 3.85 eV. (n, π^*) transitions. The third absorption band may correspond to the lowest calculated singlet-triplet transition 2.85 eV. To account for this small discrepancy we tried to obtain the phosphorescence spectrum of acrolein in cyclohexane and ethyl alcohol solutions at liquid air temperature, but failed. The *n*-hexane solution of acrolein

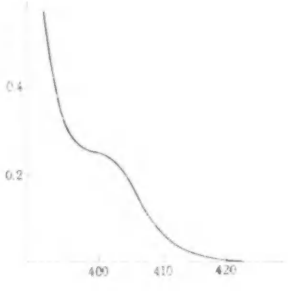


Fig. 1. Absorption band of acrolein in *n*-hexane solution (1.71 mol./l.) at 10°C.

8) H. Mackle and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 691 (1951).
9) C. C. J. Roothaan, *J. Chem. Phys.*, **19**, 116 (1951).
10) H. Kon, This Bulletin, **28**, 275 (1955).
11) J. N. Murrell and K. L. McEwen, *J. Chem. Phys.*, **25**, 1143 (1956).
12) J. W. Sidman, ibid., **27**, 429 (1957).

has an absorption maximum at 4020 Å ($\varepsilon = 0.136$, $f = 1.16 \times 10^{-7}$) as shown in Fig. 1. These values of ε and f are somewhat greater than those usually given for a singlet-triplet absorption. According to Kasha[13] it may be expected to have increased intensity in ethyl iodide solution because of the spin-orbit coupling. However, we could not observe any increase of the absorption, due to the overlapping of an intense absorption of the iodine molecule which exists in the solution. On the other hand, this band in ethyl alcohol solution showed a remarkable decrease of intensity at dry ice temperature compared with that at 10°C. Hence,

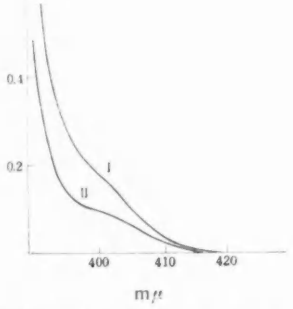


Fig. 2. The effect of temperature on the absorption band of acrolein in ethyl alcohol solution (0.956 mol./l.), curve I at 10°C, curve II at dry ice temperature.

we assigned this 4000 Å band as a hot band. Fig. 2 shows the temperature dependence of this band in ethyl alcohol solution. This weak band lies at 1226 cm^{-1} on the red side of the 0–0 band in vapor state.

The corresponding frequency could not be found in the infrared and Raman spectra[14], and we could not decide the vibrational mode of this band.

Summary

It was found that the semi-empirical method proposed by Pariser and Parr can be applied to the $n-\pi^*$ transition as well as the $\pi-\pi^*$ transition in acrolein. In acrolein the (n, π^*) triplet state is the lowest state. A weak band in the red side of the 0–0 band is a hot band and it is not the $n-\pi^*$ singlet-triplet transition band. The $n-\pi^*$ triplet band anticipated from calculation could not be found.

The author expresses his sincere thanks to Professor S. Imanishi and Dr. Y. Kanda for their kind encouragement throughout this work. He is also indebted to Dr. M. Ito and Mr. A. Sadō for their kind guidance, and also to Mr. R. Shimada for obtaining the phosphorescence spectrum of acrolein.

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13) M. Kasha, *J. Chem. Phys.*, **20**, 71 (1952).

14) K. Inuzuka, This Bulletin, to be published.

*Studies on D-Glucosamine Derivatives. VI. α-1-C-Phenyl-2-acetamido-2-deoxy-D-glucopyranoside and its Derivatives**

By Juji YOSHIMURA

(Received June 16, 1960)

The glucosylation of hydrocarbons with a carbohydrate moiety in which the pyranose ring is preserved has been accomplished by using glycosyl halides in two familiar organic reactions, i. g. the Friedel-Crafts and the Grignard reactions. Both approaches were originated by Hurd and Bonner[1] and extended by them[2]. Since then the glycosylation of organometallics has been applied to a variety of carbohydrates[3] and Grignard reagents[3-8] as well as

* Part V, This Bulletin, **33**, 1404 (1960).

1) C. D. Hurd and W. A. Bonner, *J. Am. Chem. Soc.*, **67**, 1664, 1972 (1945).

2) W. A. Bonner, Friedel-Crafts and Grignard Process, "Advances in Carbohydrate Chemistry" Vol., 6, Academic Press, Inc., New York (1951), p. 251.

3) C. D. Hurd and R. P. Holysz, *J. Am. Chem. Soc.*, **72**, 1732 (1950).

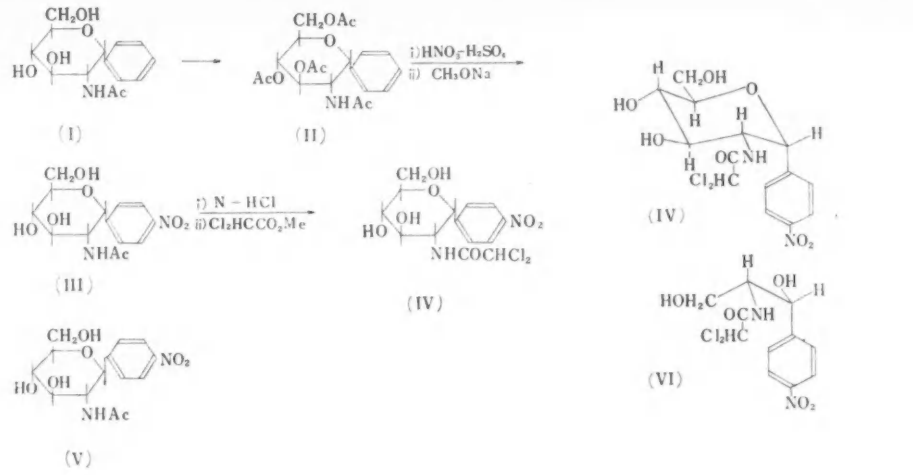
4) Yu. A. Zhdanov, L. I. Shcherbakova and T. N. Egorova, *Doklady Akad. Nauk S. S. S. R.*, **83**, 403 (1952).

5) Yu. A. Zhdanov and L. I. Shcherbakova, ibid., **90**, 185 (1953); *Chem. Abstr.*, **48**, 5114 (1954).

6) Yu. A. Zhdanov, L. I. Shcherbakova and R. V. Golovnya, *Doklady Akad. Nauk S. S. S. R.*, **107**, 259 (1956); *Chem. Abstr.*, **50**, 15476 (1956).

7) Yu. A. Zhdanov and G. F. Drofeenko, *Doklady Akad. Nauk S. S. S. R.*, **112**, 433 (1957).

8) R. Zelinski and R. E. Meyer, *J. Org. Chem.*, **23**, 810 (1958).



to organocadmium[9] and organoalkali[10] compounds. In earlier works of this series, the glycosylation of D-glucosamine was examined by the Friedel-Crafts[11] and Grignard reactions[12], and crystalline β-1-*C*-substituted-2-acetamido-2-deoxy-3, 4, 6-tri-*O*-acetyl-D-glucopyranosides (R; Me, Et, *n*-Pr, *n*-Bu, phenyl, benzyl) were obtained in the latter case. These crystalline substances were designated as β-anomers on the basis of their low rotations, and their pyranose ring systems were confirmed by periodate oxidation. The present investigation centers about the α-1-*C*-phenyl-2-acetamido-2-deoxy-3, 4, 6-tri-*O*-acetyl-D-glucopyranoside (II), produced as a by-product of the crystalline β-anomer when acetobromo-D-glucosamine hydrobromide reacts with phenylmagnesium bromide.

For the isolation of II from the crystallization mother liquors of the β-anomer, an attempt was first made to fractionate the sirupy materials obtained by concentration of the mother liquors using a magnesol-celite column. The existence of II was, however, scarcely deduced from the rotation of an effluent, though α- and β-pentaacetyl-D-glucosamine, and the β-anomer were separated in pure crystalline form. Secondly, the sirupy materials were de-*O*-acetylated by treatment with sodium in methanol and chromatographed on the same column. As is shown in Fig. 1, α-1-*C*-phenyl-2-acetamido-2-deoxy-D-glucopyranoside (I), m.p. 113~114°C, $[\alpha]_D^{24}$ 75.3°, was successfully isolated from the β-anomer and *N*-acetyl-D-glucosamine.

The proportions of the β-anomer to the α one, listed in Table II[13], are shown about ten to one in two cases. This is also ture for D-glucose derivatives[13].

On acetylation of I with acetic anhydride and pyridine, II was obtained as a thick sirup. Although all attempts to induce crystallization of this sirupy material failed, the values of elementary analysis were consistent with the theoretical values.

Nitration of II with a mixture of concentrated sulfuric and nitric acid affords again a sirupy material. However, the crystalline α-1-*C*-(*p*-nitrophenyl)-2-acetamido-2-deoxy-D-glucopyranoside (III) was obtained from it, by treating it with sodium methylate and afterwards by fractionation using a magnesol-celite column. The position of the nitro group of III was deduced from its ultraviolet absorption spectrum[14] as shown in Fig. 2.

For purposes of comparison with the compounds to be reported later, the β-anomer of III (V) was also prepared from β-1-*C*-(*p*-nitrophenyl)-2-acetamido-2-deoxy-3, 4, 6-tri-*O*-acetyl-D-glucopyranoside[14] by deacetylation.

Compound III was converted into sirupy *N*-dichloroacetyl derivative (IV) by treating with *N*-hydrochloric acid and methyl dichloroacetate in turn. The conformation at the position of *C*-1 and 2 of IV is very similar to that of chloramphenicol (VI), but IV showed no antibiotic activities.

Having several available anomeric glycosyl

9) C. D. Hurd and R. P. Holysz, *J. Am. Chem. Soc.*, **72**, 2005 (1950).
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12) J. Yoshimura, N. Muramatsu and T. Sato, ibid., **79**, 1503 (1958).
13) W. A. Bonner and J. M. Craig, *J. Am. Chem. Soc.*, **72**, 3480 (1950).
14) J. Yoshimura, T. Nakagawa and T. Sato, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 1475 (1959).

TABLE I. ISOROTATION RULE VALUES FOR ANOMERIC GLUCOSAMINE DERIVATIVES

D-Glucosamine pyranoside-derivatives		$[M]_D$	T, C	Approx. concn. g./100 ml.	Solvent	*A*	*B*
α-1-*C*-Phenyl-*N*-acetyl-		21180	24	0.65	EtOH	8790	12390
β-1-*C*-Phenyl-*N*-acetyl-		3600	20	1.0	EtOH		
α-1-*C*-(*p*-Nitrophenyl)-*N*-acetyl-		31940	22	1.0	MeOH	19395	12545
β-1-*C*-(*p*-Nitrophenyl)-*N*-acetyl-		−6850	23	0.9	MeOH		
α-1-*C*-(*p*-Nitrophenyl)-*N*-dichloroacetyl-		23710	23	0.9	MeOH	13040	10670
β-1-*C*-(*p*-Nitrophenyl)-*N*-dichloroacetyl-		−2370	27	0.8	EtOH		
N-Acetyl-α-	b)	18200	22	1.5	H_2O	11475	6725
N-Acetyl-β-	a)	−4750	22	0.054	H_2O		
Methyl *N*-acetyl-α-	c)	30800	25	1.0	H_2O	20450	10350
Methyl *N*-acetyl-β-	d)	−10100	22	2.0	H_2O		
Phenyl *N*-acetyl-α-	e)	63320	25	1.0	H_2O	33160	30130
Phenyl *N*-acetyl-β-	e)	−3060	25	1.3	H_2O		
α-1-*C*-Phenyl-*N*, *O*-tetraacetyl-		27900	25	0.7	$CHCl_3$	21650	6250
β-1-*C*-Phenyl-*N*, *O*-tetraacetyl-		−15400	20	1.2	$CHCl_3$		
N, *O*-Pentaacetyl-α-	f)	36400	20	5.0	$CHCl_3$	17965	18435
N, *O*-Pentaacetyl-β-	f)	470	20	4.3	$CHCl_3$		
Methyl *N*, *O*-tetraacetyl-α-	d)	31790	22	2.0	$CHCl_3$	19690	12100
Methyl *N*, *O*-tetraacetyl-β-	g)	−7590	20	0.3	EtOH		
Phenyl *N*, *O*-tetraacetyl-α-	e)	58330	25	2.0	$CHCl_3$	33610	24720
Phenyl *N*, *O*-tetraacetyl-β-	e)	−8890	25	2.0	$CHCl_3$		

a) R. Kuhn and F. Haber, *Ber.*, **86**, 722 (1953).
b) C. Niemann and J. T. Hays, *J. Am. Chem. Soc.*, **67**, 1302 (1945).
c) R. Kuhn, *Ber.*, **86**, 466 (1953).
d) A. Neuberger and R. P. Rivers, *J. Chem. Soc.*, **1939**, 122.
e) S. Roseman and A. Dorfman, *J. Biol. Chem.*, **191**, 609 (1951).
f) C. S. Hudson and J. K. Dale, *J. Am. Chem. Soc.*, **38**, 1431 (1916).
g) W. H. Myers and G. J. Robertson, ibid., **56**, 8 (1943).

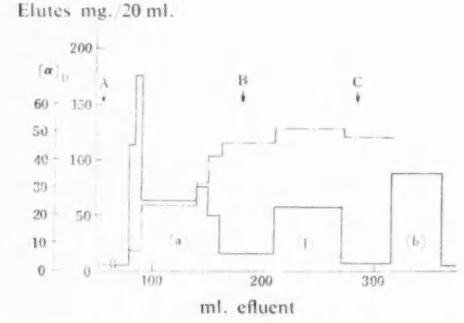

Fig. 1. Chromatographic separation of I on a magnesol-celite column.
A, B and C are a mixture of benzene and ethanol used for elution in which the ratios of benzene to ethanol are 10, 5 and 1, respectively.; ------ rotation of elutes, —— weight of elutes, (a) the β anomer of I, (b) *N*-acetyl-D-glucosamine.

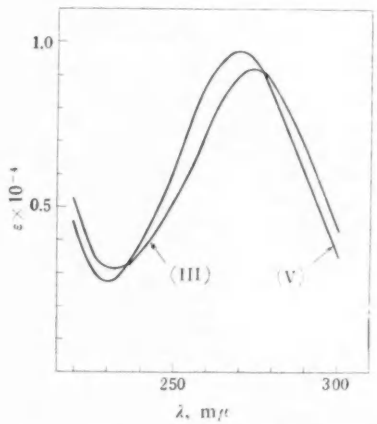

Fig. 2. Ultraviolet absorption spectra of III and V in methanol.

derivatives of D-glucosamine, it is interesting to apply Hudson's rules[15] of isorotation to them. The *A* values, referring to the molecular rotatory contribution of *C*-1 containing the phenyl group, and the *B* values, referring to the free or substituted remainder of the molecule, are presented in Table I.

For comparative purposes we have included in Table I, *B* values for other appropriately substituted anomeric D-glucosamine derivatives. Table I shows that the *A* and *B* values of glucosyl derivatives of D-glucosamine are very

15) C. D. Hudson, *J. Am. Chem. Soc.*, **31**, 66 (1909).

TABLE II. YIELDS AND RATIO OF PRODUCTS

Starting material g.		Crude yield g. (%)	Acetylderivative of the β-anomer, g.	Residual syrup, g. (β, α)	Ratio of β to α
Acetobromo-D-glucosamine hydrobromide	(5.0)	2.9 (64.0)	2.1	0.5 (0.2, 0.18)	12.8
〃	(45.0)	24.1 (59.3)	12.6	11.0 (3.69, 1.65)	9.9
α-Acetochloro-D-glucose[13]	(27.4)	19.5 (63.6)	15.0	4.2 (1.98, 1.58)	10.7

similar to that of the corresponding glucosyl derivatives of D-glucose[13], and behave almost normally.

It is interesting to compare the values A_{ph} and A_{pho} for 1-*C*-phenyl derivatives and phenyl glycosides, substances differing only in the presence or absence of an oxygen atom at *C*-1. The A_{pho} value is seen to be higher than the A_{ph} by a factor of about two to four.

Apparently, the conjugation with the aromatic nucleus of the unshared electrons on the glycosidic oxygen in the phenyl glycosides produces a considerably higher partial rotatory contribution of the *A*-portion of the molecule than is the case when the aromatic nucleus alone is present.

The substitution of the *p*-nitro group in the aromatic nucleus of 1-*C*-phenyl derivative, however, leads to an anomalously high *A* value which is analogous to that of phenyl glucosides[15].

Experimental

Reaction of Acetobromo-D-glucosamine Hydrobromide with Phenylmagnesium Bromide.—The reaction was performed in the manner described previously[12], using a ninefold increase (45 g.) in the quantities of starting material. The crude product was isolated, after acetylation, as a thick brown sirup in about 60% yield. It was crystallized from a minimum of 2-propanol, yielding β-1-*C*-phenyl-2-acetamido-2-deoxy-3, 4, 6-tri-*O*-acetyl-D-glucopyranoside. The mother liqors were concentrated to dryness, leaving a sirup which contains the α-anomer.

In Table II are tabulated two results of such preparations.

α-1-*C*-Phenyl-2-acetamido-2-deoxy-D-glucopyranoside (I).—The entire residual sirup from the second run in Table II was deacetylated with sodium in methanol. Evaporation of methanol affords 7.2 g. of sirupy materials. A part of the sirup (2.5 g.) was dissolved in 10 ml. of benzene-ethanol (10 : 1 mixture) and insoluble *N*-acetyl-D-glucosamine (0.29 g.) was filtered off. The filtrate was chromatographed at room temperature on a column packed with 25 g. of magnesol-celite (5 : 1 mixture). The solvents used for elution were benzene and ethanol of successively increasing concentrations in benzene. The effluents were examined as to the weight of elutes and their rotation. As is shown in Fig. 1, 0.98 g. of the β-anomer, 0.51 g. of the α-anomer and 0.51 g. of crystalline *N*-acetyl-D-glucosamine were obtained. The α and β anomers were again chromatographed, and 0.395 g. and 0.88 g. of pure crystals were obtained respectively. The α-anomer had m. p. 113~114°C, $[\alpha]_D^{24}$ 75.3° (*c* 0.65, chloroform).

Found: C, 59.93; H, 7.02; N, 4.63. Calcd. for $C_{14}H_{19}O_5N$(281.3): C, 59.77; H, 6.81; N, 4.98%.

α-1-*C*-Phenyl-2-acetamido-2-deoxy-3, 4, 6-tri-*O*-acetyl-D-glucopyranoside (II).—Compound I (200 mg.) was acetylated with acetic anhydride (10 ml.) and pyridine (5 ml.) at 25°C for one day. Processing in the usual manner gave 290 mg. of a clear sirup. $[\alpha]_D^{25}$ 68.5° (*c* 0.69, ethanol).

Found: C, 58.36; H, 6.45; N, 3.34. Calcd. for $C_{20}H_{25}O_8N$(407.4): C, 58.69; H, 6.18; N, 3.44%.

α-1-*C*-(*p*-Nitrophenyl)-2-acetamido-2-deoxy-D-glucopyranoside (III).—A sirupy material of II (1.5 g.) was dissolved in a mixture of 7 ml. of concentrated sulfuric acid (sp. gr. 1.8) and 7 ml. of concentrated nitric acid (sp. gr. 1.38) on cooling with ice-salt bath. After 30 min. the reaction mixture was left to stand for 1 hr. at 0°C, and for 15 min. at room temperature. About 20 ml. of dry chloroform were added and the mixture was poured gradually into ice-water including an excess amount (about 20 g.) of sodium carbonate. The chloroform layer was separated from the water layer, and the latter was extracted with chloroform in the usual manner. Evaporation of the solvent afforded about 1.5 g. of a pale yellow sirup. A small grain of sodium was added to the solution of this sirup and 15 ml. of methanol, and was left to stand for 3 hr. at room temperature. The methanol solution was diluted with 10 ml. of water and treated with 15 ml. of cation-exchanger (IRA 120) and concentrated in vacuo to dryness. The residual sirup was chromatographed on 10 g. of magnesol-celite column (5 : 1 mixture) in a manner similar to that of I shown in Fig. 1. The fractions eluted with benzene-ethanol mixtures the ratios of which were five to one and two to one were crystallized. Yield 200 mg., m. p. 170~171°C, $[\alpha]_D^{22}$ 97.5° (*c* 1.0, methanol).

Found: C, 51.18; H, 5.23; N, 8.25. Calcd. for $C_{14}H_{15}O_7N_2$(326.3): C, 51.53; H, 5.56; N, 8.59%.

α-1-*C*-(*p*-Nitrophenyl)-2-dichloroacetamido-2-deoxy-D-glucopyranoside (IV).—A mixture of 1.3 g. of III, 10 ml. of 2 N hydrochloric acid and 10 ml. of

16) W. W. Pigman, *J. Research Natl. Bur. Standards*, 33, 129 (1944).

ethanol was refluxed 3 hr. on a steam bath. The reaction mixture was concentrated in vacuo, and the residual sirup (ca. 1 g.) was neutralized with about 0.072 g. of sodium in methanol. The solution was filtered and concentrated in vacuo, and the residual sirup was refluxed in 8 ml. of *n*-butanol and 3 ml. of methyl dichloroacetate for 5 hr. The precipitate (a small amount) was filtered off, and the filtrate was concentrated to a thick sirup. An attempt was made to fractionate this on a magnesol-celite column, but no crystalline material could be obtained. The main fraction was about 0.8 g., $[\alpha]_D^{23}$ 60.0° (*c* 0.9, methanol).

Found: C, 42.88; H, 4.25; N, 7.34; Cl, 17.32. Calcd. for $C_{14}H_{16}O_7N_2Cl_2$ (395.2): C, 42.52; H, 4.08; N, 7.09; Cl, 17.94%.

β-1-*C*-(*p*-Nitrophenyl)-2-acetamido-2-deoxy-D-glucopyranoside (V).—β-1-*C*-(*p*-Nitrophenyl)-2-acetamido-2-deoxy-3, 4, 6-tri-*O*-acetyl-D-glucopyranoside (0.5 g.) was deacetylated with sodium in methanol. Processing in the usual manner gave 0.3 g. of crystals. m. p. 269~271 °C, $[\alpha]_D^{23}$ −21.0° (*c* 0.8, ethanol).

Found: C, 51.33; H, 5.47; N, 8.52. Calcd. for $C_{14}H_{15}O_7N_2$ (326.3): C, 51.53; H, 5.56; N, 8.59%.

Summary

The sirup obtained as a by-product with β-1-*C*-phenyl-2-acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-D-glucopyranoside by the action of phenylmagnesium bromide on acetobromo-D-glucosamine hydrobromide has been deacetylated and chromatographed to yield the α-anomer. Several α-derivatives have been described, among which, α-1-*C*-(*p*-nitrophenyl)-2-dichloroacetamido-2-deoxy-D-glucopyranoside which is a chloramphenicol derivative showed no antibiotic activities. The application of Hudson's rules of isorotation to the anomeric compounds in this series is discussed.

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Studies on Lactone Formation in Vapor Phase. I. Synthesis of γ-Butyrolactone

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Dehydrogenation of aliphatic glycols to the corresponding lactones with a copper catalyst was originated by Reppe[1,2] and later investigated by several investigators[3~5]. The reaction was generally carried out in the following two ways: (1) Heating glycol and a small amount of copper chromite under continuous stirring at 200~250 °C until hydrogen evolution ceased, (2) passing glycol with hydrogen over reduced copper supported on silica gel or pumice at the same temperature.

In Germany, γ-butyrolactone had been manufactured from 1,4-butanediol by the second method, and Copenhaver[6] has described its outline in "Acetylene and Carbon Monoxide Chemistry". The yield of γ-butyrolactone (90%) was satisfactory but its space time yield was very small (about 0.015).

In order to find a more active catalyst for the vapor phase catalytic dehydrogenation of 1,4-butanediol to γ-butyrolactone, the activities of reduced copper supported on various carriers, the effects of the catalyst composition, and the reaction conditions have been examined.

Experimental

Catalyst.—The catalyst consisting of 20% copper and 80% zinc oxide was prepared as follows.

An aqueous solution 300 ml. containing 51 g. of cupric nitrate trihydrate was slowly added to 300 ml. of water in which 109 g. of zinc carbonate was suspended with stirring. Stirring was continued until the deposition of basic copper carbonate on zinc carbonate with evolution of carbon dioxide had ceased. The material was then washed three times with one liter of water, filtered and dried at 70 °C. The final decomposition to copper oxide was carried out in a porcelain dish with frequent stirring and cautious heating at 300 °C until the color of the

1) W. Reppe et al., Ger. Pat., 699945 (1940); *Chem. Abstr.*, **35**, 6977 (1941).
2) W. Reppe et al., *Ann.*, **596**, 158 (1955).
3) L. P. Kyrides and F. B. Zienty, *J. Am. Chem. Soc.*, **68**, 1385 (1946).
4) R. I. Longley et al., ibid., **74**, 2012 (1952).
5) R. I. Longley et al., *Org. Synth.*, **35**, 87 (1955).
6) J. W. Copenhaver and M. H. Bigelow, "Acetylene and Carbon Monoxide Chemistry", Reinhold Publishing Corp. (1949), p. 152.

TABLE I. EFFECTS OF CARRIERS ON YIELD

Carrier	B. D.* used	Product	T. H. F.** obtained	Yield of B. L.***		B. D. recovered	Conversion
	g.	g.	g.	g.	%	g.	%
AlO(OH)	24.8	19.5	3.0	9.0	45	1.8	93
SiO_2	23.0	20.0	—	15.4	77	2.2	91
MgO	20.0	19.0	—	15.5	92	2.3	89
ZnO	23.4	22.0	—	20.9	95	0.4	98

* 1,4-Butanediol, ** Tetrahydrofuran, *** γ-Butyrolactone.

catalyst turned from light blue into dark brown.

When magnesium oxide was used as carrier, the catalyst was prepared similarly. In the case of alumina, copper hydroxide and aluminum hydroxide were coprecipitated with ammonia from the solution of copper nitrate and aluminum nitrate. In the case of silica gel, the catalyst was prepared from copper nitrate and sodium silicate by the usual manner. These catalysts were put in tablets, 8 mm. in diameter and 2 mm. in thickness. About 70 ml. of the tablets was used in each experiment.

Apparatus and Procedure. — The apparatus used is shown in Fig. 1. The dehydrogenation tube

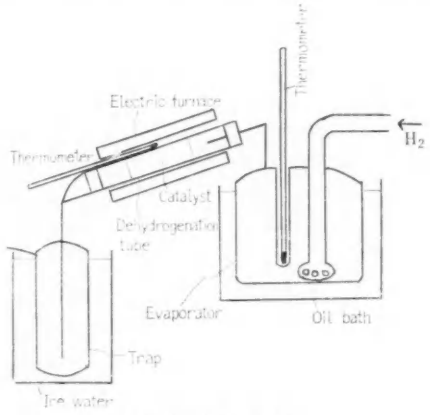

Fig. 1. Apparatus.

(60 cm.×15 mm.) was made from silica and heated in a furnace. Activation of the catalyst was carried out at 220°C in a stream of hydrogen until reduction was completed. The sample was passed in with a steady current of hydrogen. The evaporator containing 1,4-butanediol (n_D^{25} 1.4452, d_4^{25} 1.0130) was immersed in an oil bath and the feed speed of the sample was adjusted by regulating the temperature of the oil bath and rate of hydrogen. The evaporator was weighed before and after a run to determine the weight of material used. The reaction products were collected in a trap cooled by ice water, weighed and fractionated under a reduced pressure. γ-Butyrolactone (b. p. 98~100°C/25 mmHg) was easily fractionated from unreacted 1,4-butanediol (b. p. 142°C/25 mmHg). γ-Butyrolactone was a colorless liquid of n_D^{25} 1.4350, d_4^{25} 1.1264 and gave a hydrazide melting at 92°C.

Found: C, 40.92; H, 8.79. Calcd. for $C_4H_{10}O_2N_2$: C, 40.66; H, 8.53%.

Results and Discussion

Typical results for four carriers are tabulated in Table I.

The catalyst 70 ml. containing 20% copper was used. The reaction temperature was maintained at 230~240°C and the reaction time was one hour. The velocity of hydrogen passed with sample was 20 l. per hour. The yields of γ-butyrolactone were based upon the amount of butanediol consumed. With any carriers used, the conversion was very good. In the case of alumina, the yield was decreased owing to dehydration of butanediol to tetrahydrofuran. Magnesium oxide or zinc oxide was a superior carrier in respect to the yield

TABLE II. EFFECTS OF COPPER CONTENTS TO MAGNESIUM OXIDE

Cu-cont.	B. D. used	Yield of B. L.		B. D. recovered	Conversion
%	g.	g.	%	g.	%
10	25.5	20.6	96	3.0	88
20	20.0	15.5	92	2.3	89
30	23.0	19.4	95	1.6	93
40	25.0	22.0	94	0.5	98

TABLE III. EFFECTS OF COPPER CONTENTS TO ZINC OXIDE

Cu-cont.	B. D. used	Yield of B. L.		B. D. recovered	Conversion
%	g.	g.	%	g.	%
5	25.8	19.2	94	3.5	86
10	22.0	19.0	95	1.0	95
20	23.4	20.9	95	0.4	98
30	23.0	20.4	96	0.7	97
40	23.0	20.5	96	0.7	97

TABLE IV. EFFECTS OF THE REACTION TEMPERATURE

Reaction temp.	B. D. used	Yield of B. L.		B. D. recovered	Conversion
°C	g.	g.	%	g.	%
210	23.7	17.0	97	5.3	78
220	23.8	18.7	98	3.8	84
240	23.0	18.8	96	2.5	89
260	24.8	20.5	95	2.1	92
280	26.5	21.3	90	1.8	93
300	26.5	21.3	87	1.0	96
330	27.2	20.8	83	0.8	97

TABLE V. EFFECTS OF HYDROGEN VELOCITY AND LIQUID SPACE VELOCITY OF BUTANEDIOL

Velocity of H_2 l./hr.	S. V.* of H_2	Reaction time min.	B. D. used g.	L. S. V.** of B. D.	Yield of B. L. g.	Yield of B. L. %	S. T. Y.*** of B. L.	B. D. recovered g.	Conversion %
10	145	70	25.2	0.34	21.2	92	0.26	1.0	96
20	290	60	24.0	0.34	19.4	95	0.28	2.5	90
30	435	60	23.5	0.34	18.2	93	0.26	3.0	87
20	290	120	26.0	0.19	21.0	92	0.15	2.0	92
20	290	40	26.0	0.57	18.5	96	0.40	5.8	78
10	145	120	23.7	0.17	19.0	87	0.14	0.8	97
30	435	40	27.3	0.58	19.0	93	0.41	6.0	77

* Space velocity, ** Liquid space velocity, *** Space time yield.

and undesirable side reaction. These catalysts were prepared by the new method described in the experimental part.

Effects of the catalyst composition, relative ratio of copper to magnesium oxide and to zinc oxide, are shown in Tables II and III, respectively. The reaction conditions were the same as those in Table I. The suitable contents of copper were about 10~20%. The higher contents of copper did not improve the yield and conversion. Effects of the reaction temperature in the case of 20% copper-zinc oxide is shown in Table IV. The reaction time and the hydrogen velocity were the same as those of the above experiments. The conversion increased with the elevation of the reaction temperature and γ-butyrolactone was obtained in a good yield at 210~260°C. At above 280°C the product decreased owing to undesirable decompositions.

Finally, in use of the same catalyst as the above, effects of space velocity of hydrogen and liquid space velocity of butanediol on yield, space time yield and conversion were examined at 230~240°C and the results were summarized in Table V.

The yield was hardly affected with varying velocity of hydrogen and butanediol, but the long contact with the catalyst lowered the yield to some extents. With increase of liquid space velocity from 0.17 to 0.58, the space time yield increased from 0.14 to 0.41, but the conversion decreased from 97% to 77%.

No final information was yet available as to the life of the catalyst, but its activity hardly decreased after several hours.

Summary

Vapor phase catalytic dehydrogenation of 1, 4-butanediol to γ-butyrolactone with reduced copper supported on various carriers was studied. It was found that copper supported on zinc oxide or magnesium oxide was a superior catalyst. In the case of a catalyst consisting of 20% copper and 80% zinc oxide, the yield and space time yield of γ-butyrolactone were 95% and 0.28 at 230~240°C, respectively.

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Studies on Leucomycin. IV. Isolation of Mycaminose from the Acid Hydrolysate

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Recent studies in this laboratory have demonstrated that the leucomycin complex produced by Streptomyces kitasatoensis Hata[1-3], can be resolved into six basic antibiotics by elution chromatography[4] or by counter current distribution[5]. The present paper will describe the presence of a mycaminose residue[6] as the basic moiety in each leucomycin component. Leucomycin A1 ($C_{46}H_{81}NO_{17}$, m. p. 135~138°C), the main component of this antibiotics complex, possessed a pK_a' of 7.1 and did not reduce Fehling's solution. It gave no color with carbohydrate reagents such as anthrone under the usual conditions[7]. Upon hydrolysis with 2 N hydrochloric acid at 100C°, however, there was produced an appreciable amount of reducing sugars which became colored with sulfuric acid-anthrone reagent[8], together with some humic substances. By the elution chromatography of the hydrolysate from a column of Dowex-50 of H-phase with 2 N hydrochloric acid, the anthrone reaction-positive components were separated into three fractions, as shown in Fig. 1. The first fraction possessed no nitrogen, while the second fraction (IIa) contained a basic sugar, which was crystallized as a hydrochloride ($C_8H_{17}NO_4$·HCl, m. p., 114~116°C) from the alcoholic solution by the addition of ether.

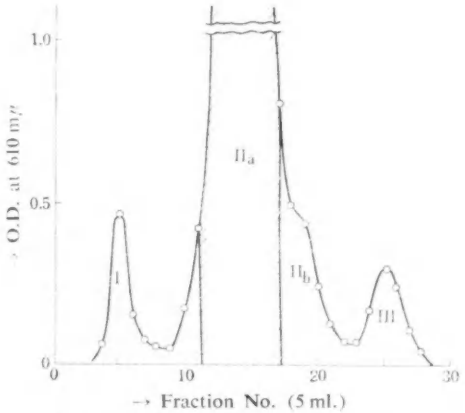

Fig. 1. Elution chromatogram of sugar components derived from leucomycin A1 with hydrochloric acid. The acid hydrolysate corresponding to 20 g. of leucomycin, was eluted from a column of Dowex-50 (H-phase) of 1×30 cm. with 2 N hydrochloric acid. The concentration of sugar was determined photocolorimetrically with sulfuric acid-anthrone reagent[8].

This basic sugar rapidly consumed one mole of slight alkaline iodine at room temperature, indicating that it was an aldose[9].

The aldose possessed one *C*-methyl group and showed a characteristic iodoform reaction, too. By the action of 3 N sodium hydroxide at 50°C, the basic group of this aldose was easily split as dimethylamine, which was identified as 2, 4-dinitro-*N*-dimethyl aniline after coupling with 1-fluoro-2, 4-dinitrobenzene[10]. These results seemed to indicate that the basic sugar isolated from leucomycin A1 was an aldomethylpentose having a dimethylamino group.

As shown in Fig. 2, the dimethylamino-aldomethylpentose consumed 4 mol. of periodate in aqueous solution at room temperature : one

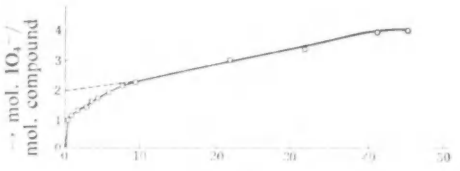

Fig. 2. Periodate consumption by the basic sugar isolated from leucomycin A1.

1) T. Hata et al., *J. Antibiotics Ser.*, **A6**, No. 2, 87 (1953).
2) T. Hata, F. Koga and H. Kanamori, ibid., **A6**, No. 3, 109 (1953).
3) J. Abe, Y. Suzuki, T. Watanabe and K. Satake, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 969 (1960).
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5) T. Watana,de H. Nishida and K. Satake, ibid., **33**, 1104 (1960).
6) F. A. Hochstein and P. P. Regar, *J. Am. Chem. Soc.*, **77**, 3033 (1955).
7) Y. Sano, T. Hoshi and T. Hata, *J. Antibiotics, Ser.*, **A7**, No. 3, 88 (1954).
8) D. L. Morris., *Science*, **107**, 254 (1948).
9) G. L. Miller and A. L. Burton, *Anal. Chem.*, **31**, 1790 (1959).
10) F. Sanger, *Biochem. J.*, **39**, 507 (1945).

mole very rapidly, one mole with moderate speed, and the additional two moles very slowly. During the initial stage of the oxidation, formic acid was produced at a rate approximating one mole per mole of periodate consumed: while the formation of acetaldehyde which was identified as the 2,4-dinitrophenylhydrazone and assayed photocolorimetrically with *p*-hydroxydiphenyl[11], was observed mainly during the second stage of oxidation. During the final stage of the oxidation, there was observed the formation of dimethylamine and an increase of the amount of formic acid with the increase of periodate consumption. No formation of formaldehyde was confirmed with the use of chromotropic acid[12]. These results suggested that the basic sugar possessed the following structure.

The first stage The second stage

$$CHO\text{-}CHOH\text{-}CHN(CH_3)_2\text{-}CHOH\text{-}CHOH\text{-}CH_3$$

The third stage

As already described in the present paper, the dimethyl amino group of this sugar was rather easily split as dimethylamine under the action of alkali. Fig. 3 illustrates the velocity of liberation. As a control, was used C_7-dimethylamino aldose, which had been derived from the original C_8-sugar with the action of one mole of periodate (presumably possessing methyltetrose structure[6,9]; see Fig. 2). A marked difference observed between the stabilities of both dimethylamino sugars in alkaline solution, seemed not to be inconsistent with the structure presumed above; thus the original C_8-sugar possessed the dimethylamino group at the β-position, while the oxidation product possessed it at the α-position from the aldehyde group, respectively. As to the steric configuration of the 3,6-deoxy-3-dimethyl amino aldohexose isolated from leucomycin A1, the present author had no experimental data. The physical constants of this sugar, however, were very close to those reported on a 3,6-deoxy-3-dimethylaminoaldohexose, mycaminose which had been previously obtained from the acid hydrolysate of magnamycin and the infrared absorption spectra of both sugars were essentially the same, as shown in Fig. 4. These results indicated that mycaminose was a basic moiety of leucomycin A1.

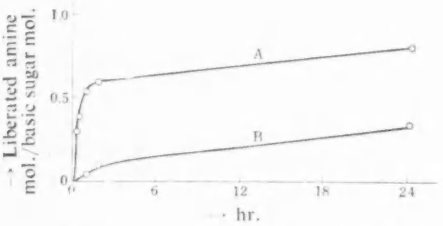

Fig. 3. Liberation of dimethylamine from dimethylamino sugar under the action of 3 N sodium hydroxide at 50°C.
A: CHO-CHOH-CHN$(CH_3)_2$-CHOH-CHOH-CH_3 from leucomycin A1.
B: CHO-CHN$(CH_3)_2$-CHOH-CHOH-CH_3 derived from A with the action of one mole of periodate.
The amount of dimethylamine was determined spectrophotometrically, after the coupling with 1-fluoro-2,4-dinitrobenzene.

It should be emphasized here that pK_a' value of mycaminose (8.1) was somewhat higher than that of intact leucomycin A1 (7.1). Such a difference between their pK_a' values may suggest that the hydroxyl group adjacent to the dimethylamino group of mycaminose residue in intact leucomycin A1, was blocked with other groups in the same way as magnamycin[13]. The pK_a' of leucomycin, magnamycin, and their related compounds are listed in Table I.

Other components of leucomycin, A2 ($C_{65}H_{111}NO_{22}$, m. p., 142~144°C), B1 ($C_{35}H_{59}NO_{13}$,

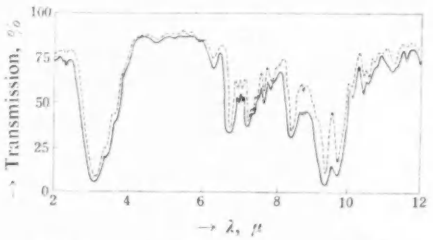

Fig. 4. Infrared absorption spectra of the basic sugars from leucomycin A1 and from magnamycin.

TABLE I. pK_a' OF LEUCOMYCIN, MAGNAMYCIN AND THE RELATED COMPOUNDS

	Leucomycin		Magnamycin
	A1, A2	B1, B2, B3, B4	
Intact antibiotics	7.1	6.6~6.8	7.0
Basic sugar obtained with 6 N HCl hydrolysis	8.1		8.1
A basic moiety obtained with methanolysis	8.1*	7.8*	8.3

* T. Watanabe, unpublished.

11) B. A. Neidig and W. C. Hess, *Anal. Chem.*, **24**, 1627 (1952).
12) M. J. Boyd and M. A. Logan, *J. Biol. Chem.*, **146**, 279 (1942).
13) R. B. Woodward, *Angew. Chem.*, **68**, 13 (1956).

m. p., 214.5~216.5°C), B2 ($C_{38}H_{65}NO_{16}$, m. p., 214~216°C), B3 ($C_{34}H_{53}NO_{13}$, m. p., 216~217°C), B4 ($C_{38}H_{59}NO_{16}$, m. p., 221~223.8°C), also gave a basic sugar which was absorbed on a column of Dowex-50 of H-phase, on their acid hydrolysis. Although the isolation of the basic sugar in preparative scale was impossible, due to the limited amounts of these minor antibiotics, the paper chromatographic R_f values was just the same as that of mycaminose and differed from that of desosamine which had been reported as another basic moiety of macrolides[14,15].

Experimental

Leucomycin.—The leucomycin complex used in this experiment, was a commerical bulk, Lot No. 9LM-44, which was kindly offered from the Research Institute, Toyo Jozo Co. Ltd. Leucomycin components, A1, A2, B1, B2, B3 and B4, were isolated from the complex by the previous fractionation with benzene, followed by the further minute resolution with the use of counter current distribution technique, as already reported by the present author[5].

Isolation of Basic Sugar from the Acid Hydrolysate of Leucomycin A1.—Twenty grams of leucomycin A1 (m. p. 135~138°C, Found: C, 60.99; H, 8.72; N, 1.52. Calcd. for $C_{46}H_{81}NO_{17}$: C, 60.13; H, 8.75; N, 1.54%.) were disolved into 300 ml. of 2 N hydrochloric acid, and the solution was heated at 100°C for 3 hr. The dark brown solution so produced, after repeated washing with chloroform (five times, 30 ml. each) to remove humic substances, was concentrated to syrup under reduced pressure. The residue, dissolved in 10 ml. of water, was added to a column of Dowex-50 (H-phase, 150~200 mesh) of 1×30 cm. As soon as the applied sample solution had been allowed to flow into the column, elutions with 50 ml. of water, then with 2 N hydrochloric acid were initiated. Throughout these procedures, the rate of flow was maintained to be 10±2 ml. per hour. The concentration of sugar in the effluent, which had been collected in 5 ml. fractions by means of an automatic fraction collector, was determined spectrophotometrically with sulfuric acid-anthrone reagent, as follows. A half millilitre of the solution to be analyzed was mixed with 2 ml. of 2 per cent anthrone in concentrated sulfuric acid, and the mixture was heated for 15 min. in boiling water bath. The optical density of the resulting blue color was measured at 610 mμ.

The combined fractions, corresponding to the second main peak component (from No. 11 to No. 16; see Fig. 1), were concentrated to dryness under reduced pressure. The crystalline residues were dissolved into a minute amount of ethyl-alcohol and recrystallized out by the addition of ether. m. p. 114~116°C $[\alpha]_D^{25}$ −30° (c 1 in water 24 hr.) Yield 2.8 g.

Found: C, 42.18; H, 8.09; N, 5.94. Calcd. for $C_8H_{17}NO_4 \cdot HCl$: C, 42.19; H, 7.81; N, 5.59%.

Periodate Oxidation of the Basic Sugar Isolated from Leucomycin A1.—The oxidation was achieved in 0.1 per cent acetic acid at 25°C, with the uses of 3~7 mM of basic sugar hydrochloride and of 25~30 mM sodium metaperiodate, and an aliquot of the reaction mixture was pipetted out after a definite period, for the following analysis. The periodate consumption was determined, after the addition of potassium iodide by the titration with thiosulfate, and the amounts of acetaldehyde and of formaldehyde were determined spectrophotometrically with *p*-hydroxybiphenyl-[11] and chromotropic acid-[12] reagents, according to the method described in the cited reference, respectively. The amount of formic acid was assayed by the alkali-titration, on the oxidation mixture in aqueous solution instead of 0.1 per cent acetic acid solution. Acetaldehyde, formic acid, and dimethylamine produced by the periodate oxidation, were identified as the 2,4-dinitrophenylhydrazone (m. p. 160~161°C), *p*-bromophenacyl ester (m. p. 100~101°C) and dinitrophenyl derivative (m. p. 78°C), respectively.

Alkali Degradation of the Basic Sugar from Leucomycin A1.—Four hundred milligrams of the basic sugar hydrochloride was dissolved into 25 ml. of 3 N sodium hydroxide at 45°C. A 5 ml. portion of the solution, after a definite period, was immediately cooled and neutralized, and dinitrophenylated with 1-fluoro-2, 4-dinitrobenzene according to the method of Sanger[10].

The dinitrophenylation mixture, was directly added to a column of Amberlite IRC-50 of H-phase (100~150 mesh, 1×20 cm.)[16] and the column was washed with water. The unreacted reagent and 2,4-dinitrophenol, a main by-product, were removed in the filtrate and the washing. 2, 4-Dinitro-*N*-dimethylaniline derived from dimethylamine, was then eluted from the column with a mixture of acetone and water (1 : 1 *V/V*) and the amount was determined by the spectrophotometry at 380 mμ. The absorption spectrum of the effluent was essentially the same as that of the authentic specimen in a wavelength range between 250 to 450 mμ.

As a control, a reaction mixture derived from the basic sugar with the equimolecular amount of sodium periodate (see Fig. 2) was used.

Other Analysis of the Basic Sugar Isolated from Leucomycin.—Aldose-reaction with alkaline iodine[9] 2-deoxyaldose reaction with perchloric acid-vanilline reagent[17], dinitrophenylation with 1-fluoro-2,4-dinitrobenzene for the detection of primary and secondary amino groups[10], were achieved under the conditions reported in the references cited, respectively.

Paper-chromatographic analysis was performed by the usual ascending method, with the uses of isopropanol-pyridine-acetic acid-water (8 : 8 : 1 : 4 *V/V*), *n*-butanol-pyridine-water (6 : 4 : 5 *V/V*) and collidine-pyridine-water (2 : 1 : 1 *V/V*) as the solvent

14) R. K. Clark, Jr., *Antibiotics and Chemotherapy*, **3**, 663 (1953).
15) C. Djerassi and A. Bowers, *J. Am. Chem. Soc.*, **78**, 1729 (1956).
16) T. Seki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **75**, 1297 (1954).
17) A. P. MacLennan, H. M. Randall and D. W. Smith, *Anal. Chem.*, **31**, 2020 (1959).

systems. Ammonial silver nitrate was used for the detection of the spot, in both cases.

The author desires especially to thank Professor K. Satake for his constant support and encouragement throughout this work, and also gratitude to Mr. S. Kurioka and Mr. K. Fujii for their assistance.

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Polyaddition Reaction of Diphenylsilane to Diallyl Carboxylate

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The monofunctional addition reaction of phenylsilane or methyl diethoxysilane to allyl acetate was first studied by Speier and coworkers[1,2], and 3-(phenylsilyl) propyl acetate and 3-(diethoxy methylsilyl)propyl acetate were prepared by this method under the influence of *tert*-butyl hydroperoxide. The addition reaction of trichlorosilane and methyl dichlorosilane to allyl acetate was also studied under the influence of platinum catalyst[3].

As an example of the bifunctional addition reaction, we have reported in the previous short communication, the polyaddition reaction of diphenylsilane to diallyl phthalate[4].

In the present work we have tried to extend the reaction in order to obtain larger molecules which might have more interesting properties. Some experiments using diallyl phthalate and diphenylsilane at various reaction conditions (reaction temperature, catalyst concentration and monomer concentration) are summarized in Tables II—VI.

The new method of polymer synthesis was further extented to the polyaddition reaction of diphenylsilane and the following diallyl carboxylate : diallyl oxalate, malonate, succinate, adipate, sebacate, phthalate, isophthalate and terephthalate.

Experimental

Materials.—*Diphenylsilane.*—Diphenylsilane was prepared from diphenyldichlorosilane and lithium aluminum hydride by ordinary method[5]. Three hundred and four grams (1.2 mol.) of diphenyldichlorosilane was added to 25 g. (0.68 mol.) of lithium aluminum hydride in 300 ml. of anhydrous ether. The solution was refluxed for several hours and hydrolyzed with 260 ml. of dilute hydrochloric acid. The ethereal layer was distilled to give 215 g. of diphenylsilane b. p. 109°C/7 mmHg, n_D^{20} 1.5799, d_4^{20} 0.9970.

Diallyl Phthalate.—The commercial product was distilled under reduced pressure before use. The portion boiling at 155°C/6 mmHg, n_D^{20} 1.5205, d_4^{20} 1.1205, was used in the polyaddition reaction.

Other Diallyl Carboxylates.—Diallyl carboxylates were prepared by the method described previously[6]. Their physical properties were listed in Table I.

TABLE I. PHYSICAL PROPERTIES OF DIALLYL CARBOXYLATES

Diallyl carboxylates	B. p. °C/mmHg	n_D^0	d_4^0
Oxalate	104～106/15	1.4470	1.0890
Malonate	115/4	1.4480	1.0643
Succinate	112～113/8	1.4514	1.0559
Adipate	136～138/8	1.4539	1.0226
Sebacate	181～183/9	1.4564	0.9788
Phthalate	155/6	1.5205	1.1205
Isophthalate	163/8	1.5250	1.1213
Terephthalate	166～167/8	—	—

Catalyst.—Prepared by dissolving 0.518 g. of commercial $H_2PtCl_6 \cdot 6H_2O$ (10^{-3} mol.) in 100 ml. *tert*-butyl alcohol.

Polyaddition Reaction.—To the equimolar mixture of diphenylsilane, and to diallyl carboxylate in a glass tube was added a constant amount of chloroplatinic acid solution. The tube was then sealed in a nitrogen atmosphere, and heated for several hours in a dry oven of constant temperature. The reaction product was dissolved in 100 ml. of acetone, and filtered. To the filtrate 30 ml. of water was added and reprecipitated. The precipitates were separated by decantation and dried in a vaccum desiccator at 50°C for 7 days until it reached constant weight.

Determination of Molecular Weight.—The molecular weight was calculated from the freezing point depression in benzene.

1) J. L. Speier et al., *J. Am. Chem. Soc.*, **78**, 2278 (1956).
2) J. L. Speier et al., ibid., **79**, 974 (1957).
3) L. G. Goodman et al., ibid., **79**, 3073 (1957).
4) K. Kojima., This Bulletin, **31**, 666 (1958).
5) R. A. Benkeser et al., *J. Am. Chem. Soc.*, **74**, 648 (1952).
6) K. Kojima et al., *Reports of the Research Institute of Dental Materials Japan*, **8**, 136 (1957).

Determination of Inherent Viscosity.—One fifth of a gram of solvent free polymer was dissolved in 50 ml. of benzene and the viscosity was determined by an Ostwald type viscosimeter at 25°C.

Results and Discussion

The preliminary experiment for determing conditions which favor formation of polyaddition products were carried out using diphenylsilane and diallyl phthalate.

Temperature Dependence.—Polymerization of diphenylsilane with diallyl phthalate was carried out at various temperatures. The results are given in Tables II, III and IV.

The largest polymer was prepared at 120°C, 48 hr. and 0.1 ml. catalyst. The degree of polymerization increased as the conversion became higher. Higher reaction temperature also seemed to increase the degree of polymerization. It became clear that the addition reaction was of second order at the initial stage (Figs. 1 and 2), and the k values were $k_{80}=2.5$, $k_{100}=5.2$ and $k_{120}=13.2\times10^{-5}$ g./sec. mol. When the logarithm of the initial rates of polymerization was plotted against reciprocals of temperatures ($1/T$), a good straight line was obtained (Fig. 3). The over-all activation energy calculated from the slope in

Table II. Polyaddition reaction of diphenylsilane with diallyl phthalate at 80°C

Reaction time, hr.	Conversion %	Mol. wt.	$[\eta]$
3	3.5	421	0.5
6	5.1	482	0.5
12	9.8	718	0.6
24	17.9	789	0.6
48	24.8	877	0.6

Diphenylsilane 4.519 g., diallyl phthalate 6.041 g. and catalyst 5×10^{-5} mol./ml. were used.

Table III. Polyaddition reaction of diphenylsilane with diallyl phthalate at 100°C

Reaction time, hr.	Conversion %	Mol. wt.	$[\eta]$
3	5.2	498	0.5
6	9.7	663	0.6
12	18.8	880	0.6
24	31.9	1288	0.7
48	46.4	1394	0.7

Diphenylsilane 4.519 g., diallyl phthalate 6.041 g. and catalyst 5×10^{-5} mol./ml. were used.

Table IV. Polyaddition reaction of diphenylsilane with diallyl phthalate at 120°C

Reaction time, hr.	Conversion %	Mol. wt.	$[\eta]$
3	10.9	510	0.6
6	22.9	783	0.6
12	34.7	1079	0.6
24	55.9	1583	0.7
48	70.6	1688	0.7

Diphenylsilane 4.519 g., diallyl phthalate 6.041 g. and catalyst 5×10^{-5} mol./ml. were used.

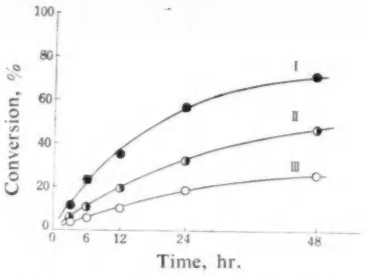


Fig. 1. Correlation of conversion percent with time.
I for reaction temperature 120°C (●), II for 100°C (◑), III for 80°C (○).

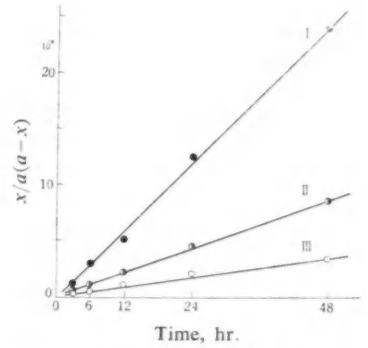


Fig. 2. Correlation of $x/a(a-x)$ with time.
I for reaction temperature 120°C (●), II for 100°C (◑), III for 80°C (○).

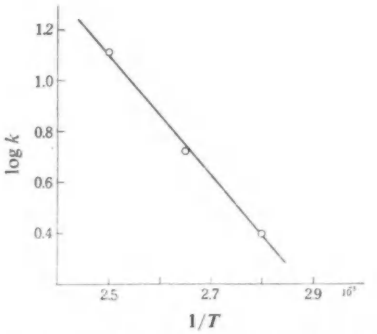


Fig. 3. Correlation of $\log k$ with $1/T$.

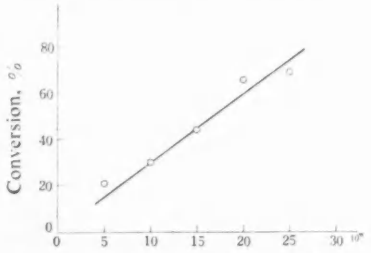
Fig. 3 was found to be 12 kcal./mol. for this reaction.

Effect of the Catalyst Concentration. — The data for the effect of the catalyst concentration is given in Table V, and the dependence of the initial rate of polymerization upon the concentration of catalyst are shown in Fig. 4.

TABLE V. EFFECTS OF CATALYST CONCENTRATION IN ADDITION REACTION OF DIPHENYLSILANE WITH DIALLYL PHTHALATE

Catalyst conc. mol./ml.	Conversion %	Mol. wt.	$[\eta]$
5×10^{-3}	21.2	758	0.6
10	29.7	836	0.6
15	44.9	746	0.6
20	65.5	660	0.6
25	68.6	773	0.6

Diphenylsilane 4.519 g., diallyl phthalate 6.041 g. were used and were heated at 110°C., 6 hr.



Catalyst concentration, mol./ml.

Fig. 4. Effect of catalyst concentration.

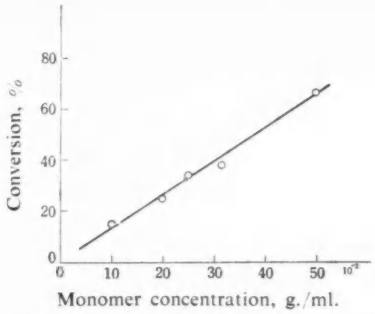
It is evident that the initial rate of polymerization is proportional to the concentration of chloroplatinic acid solution. The molecular weight of the polymer, however, is almost independent of the concentration of the catalyst.

Effect of Initial Monomer Concentration. — The relationship between initial rate of polymerization and the concentration of diphenylsilane-diallyl phthalate mixture in toluene

TABLE VI. EFFECTS OF INITIAL MONOMER CONCENTRATION IN ADDITION REACTION OF DIPHENYLSILANE WITH DIALLYL PHTHALATE

Monomer conc. g./ml.	Conversion %	Mol. wt.	$[\eta]$
50×10^{-2}	66.3	870	0.6
33	36.7	627	0.6
25	33.5	597	0.5
20	24.6	545	0.5
10	15.5	463	0.5

Diphenylsilane 4.519 g., diallyl phthalate 6.041 g. and catalyst 20×10^{-3} mol./ml. were used and were heated at 110°C, 24 hr.



Monomer concentration, g./ml.

Fig. 5. Effect of initial monomer concentration.

was studied at 110°C. The data for the rate of diminution of monomer concentration are given in Table VI and Fig. 5.

It is clear that the initial rate is proportional to the concentration of diphenylsilane—diallyl phthalate mixture.

The above result indicates that the over-all rate of polyaddition reaction, k_p of diphenylsilane with diallyl phthalate is proportional to the initial monomer concentration (M) and to the catalyst concentration (C).

$$k_p \propto (M)(C)$$

The molecular weight of the polymer is proportional to the initial monomer concentration, but independent of the catalyst concentration.

Polyaddition Reaction of Diphenylsilane to Diallyl Carboxylates. — Similar experiments of diphenylsilane to diallyl oxalate, malonate, succinate, adipate, sebacate, phthalate, isophthalate, and terephthalate were carried out. The results obtained are shown in Table VII.

TABLE VII. ADDITION REACTION OF DIPHENYLSILANE WITH DIALLYL CARBOXYLATES

Diallyl carboxylate	Conversion %	Mol. wt.	$[\eta]$	Si Calc. %	Si Found %
Oxalate	27.5	650	0.6	7.93	8.64
Malonate	59.5	990	0.6	7.62	7.36
Succinate	64.9	1080	0.6	7.34	7.38
Adipate	55.8	1120	0.6	6.84	7.58
Sebacate	76.3	1170	0.6	6.02	5.45
Phthalate	73.6	1860	0.7	6.52	6.24
Isophthalate	66.5	—	—	6.52	6.49
Terephthalate	53.0	—	—	6.52	6.35

Diallyl carboxylate 0.02 mol. and diphenylsilane 0.02 mol. were used and were heated at 110°C, 50 hr.

Addition products were viscous oily liquids, but the adducts of diphenylsilane to diallyl phthalate and isophthalate and terephthalate

were light yellow, glassy solid, and were useful as adhesives. Their softening temperatures were ca. 108°, 120°and >200°C.

Summary

The polyaddition reaction of diphenylsilane to diallyl phthalate was studied. The reaction was found to be of the second order at the initial stage. The over-all rate is proportional to the initial monomer and catalyst concentration. The over-all activation energy calculated for this reaction was found to be 12 kcal./mol. at 80~120°C.

By a similar method following polyesters have been prepared from diphenylsilane and diallyl carboxylates: Polydiphenylsilylene 3, 3'-bis(trimethylene)oxalate, malonate, succinate, adipate, sebacate, phthalate, isophthalate and terephthalate. Their molecular weight and inherent viscosity were determined and properties have been described.

The author is much indebted to Professor Yoshio Iwakura for his many useful suggestions and to Mr. Niro Tarumi for his help in the experiments. Appreciation is also expressed to Shin-etu Chem. Co. for their kindness in supplying the diphenyldichlorosilane.

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Absorption Spectra of Unstable Colored Intermediates from Picryl Chloride by the Action of Sodium Hydroxide

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(Received July 9, 1960)

In a previous paper[1], it was reported that on treatment of an aqueous solution of picryl chloride with a drop of aqueous solution of sodium hydroxide, a red solution was instantaneously formed and in a few minutes changed into a yellow solution which showed a spectrum closely resembling a spectrum of picric acid. At room temperature the red color faded away so fast that its spectrum could not be measured. It has, however, been found that the red solution containing a small quantity of ethanol is relatively stable. An attempt has, therefore, been made to measure the spectrum of the red solution prepared by adding a sodium hydroxide solution to an aqueous picryl chloride solution containing a small quantity of ethanol, together with spectra of colored solutions of picryl chloride in ethanol and in acetone in the presence of sodium hydroxide. These spectra have been compared to investigate a solvent effect on them.

Experimental

Picryl chloride of Tokyo Kasei Co. guaranteed grade was recrystallized twice from methanol-water; m. p. 82.5°C (lit. 83°C). Commercial pure picric acid was recrystallized three times from water; m. p. 122.6°C (lit. 122.5°C). Commercial guaranteed ethanol and acetone were fractionally distilled after usual treatments. The spectra of the solutions were measured with a Hitachi EPU-2 spectrophotometer at room temperature. Path length of absorption celles was 1 cm.

Results and Discussion

Absorption Spectra of the Red-Colored Solution in Water Containing a Small Quantity of Ethanol. — The orange aqueous solution of picryl chloride was made by pipetting 1 cc. of an aqueous sodium hydroxide solution and 5 cc. of ethanol into 1 cc. of a paleyellow ethanolic solution of picryl chloride and diluting the solution with water to 25 cc. The orange solution changed into a paleyellow solution by addition of a dilute aqueous solution of hydrochloric acid immediately after the preparation. When it was allowed to stand at room temperature, the orange solution changed gradually into a yellow solution. The spectra of the orange solution are shown in Fig. 1. Picryl chloride in water, in ethanol and in acetone dose not show an absorption maximum in a range of wavelengths from 300 mμ to 600 mμ[1]. The orange solution gives absorption bands at about 360, 416 and 490 mμ immediately after the preparation, but an only intense absorption band at about 397 mμ when the solution is allowed to stand at room temperature for more than six hours.

1) T. Abe, This Bulletin, 32, 339 (1959).

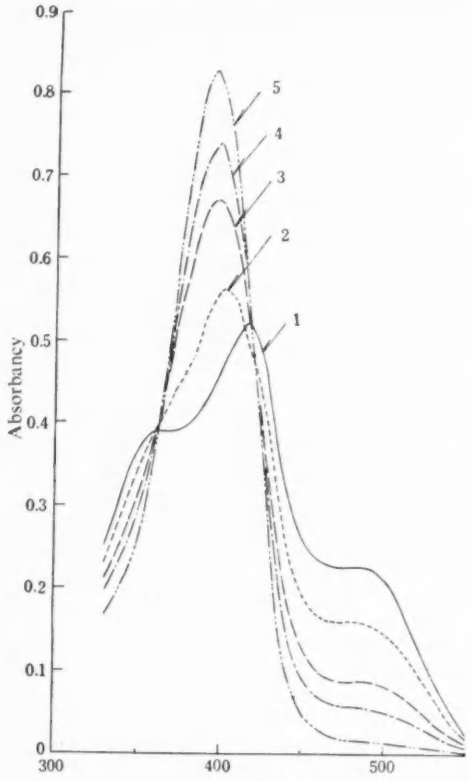


Fig. 1. Absorption spectra of picryl chloride (3.15×10^{-5} mol.) in water containing ethanol (24% by volume) in the presence of sodium hydroxide (0.377 N) at room temperature.
1 immediately after the preparation,
2 after 2.5 hr.,
3 after 6 hr.,
4 after 9 hr.,
5 after 20 hr.

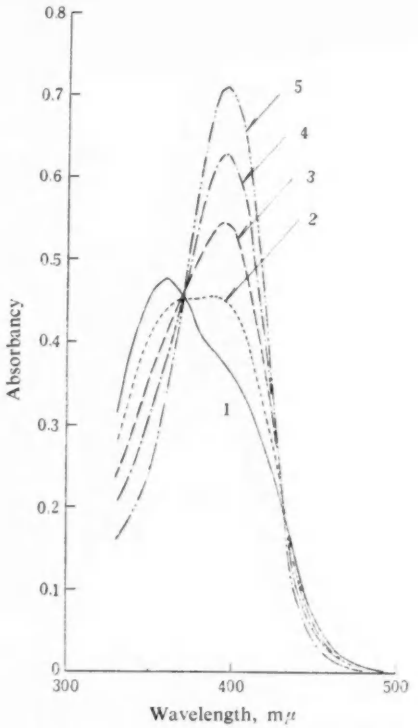


Fig. 2. Absorption spectra of picric acid (3.12×10^{-5} mol.) in water containing ethanol (24% by volume) in the presence of sodium hydroxide (0.377 N) at room temperature.
1 immediately after the preparation,
2 after 2 hr.,
3 after 5 hr.,
4 after 9 hr.,
5 after 20 hr.

Spectra of a solution of picric acid under the same condition in which the orange aqueous solution of picryl chloride was prepared, are indicated in Fig. 2. The solution of picric acid shows absorption bands at about 360 and 400 mμ, due to picrate anion, immediately after the preparation. However, when it is allowed to stand for many hours, the solution gives a 396 mμ band similar to the absorption curves 3-5 in Fig. 1. On addition of an aqueous hydrochloric acid solution, the 396 mμ band of the solution of picric acid disappears, as indicated in Fig. 3. Neither a spectrum of an aqueous picric acid solution (3.12×10^{-5} mol.) only in the presence of sodium hydroxide of 0.377 N nor a spectrum of an aqueous picric acid solution (3.12×10^{-5} mol.) containing only 24% ethanol by volume changed at all, although the solutions were allowed to stand at room temperature for more than ten hours. The intense 396 mμ bands in Fig. 2 closely resemble those of aqueous concentrated sodium hydroxide solutions of picric acid[2]. Both of the latter also disappeared when hydrochloric acid was added to the solutions. Accordingly, the 396 mμ bands in Fig. 2 may be due to a complex between picric acid and sodium hydroxide.

From the above results, the 397 mμ band of the solution in Fig. 1 can be considered to be due to picric acid produced from picryl chloride, in water containing both ethanol and sodium hydroxide. The 360 mμ band of the absorption curve 1 in Fig. 1 appears to be

2) T. Abe, *Nature*, **187**, 234 (1960).

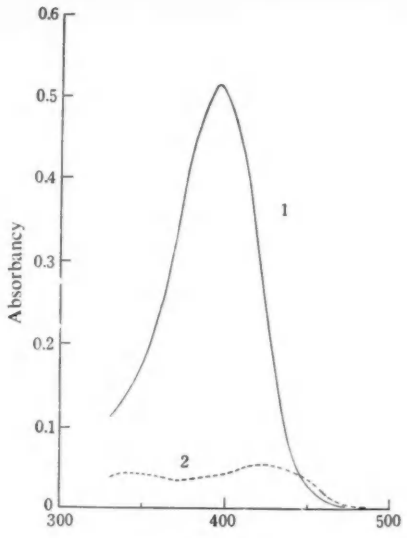
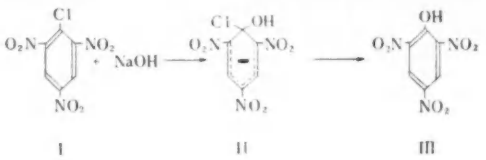


Fig. 3. Absorption spectra of solutions obtained by adding 2 cc. of water and 2 cc. of an aqueous hydrochloric acid solution (6.24 N), respectively, to 5 cc. of the solution of Fig. 2, stood for 25 hr.
1 water,
2 hydrochloric acid.

due to picric acid that changes later into the complex giving the 397 mμ band. Therefore, the 416 and 490 mμ bands of the curve 1 in Fig. 1 can be considered to be due to an labile intermediate that appears in the process of the substitution reaction of picryl chloride (I) to picric acid (III). This intermediate may be expected to be the same addition product II of Meisenheimer's type as presented for many colored products of polynitrobenzene derivatives with alkalies[1-15].



(red-colored)

The absorption curve 1 at 416 and 490 mμ in Fig. 1 closely resemoles those of red aqueous solutions of 1, 3, 5-trinitrobenzene, 2, 4, 6-trinitrotoluene and tetryl in the presence of sodium hydroxide[1-5]. The intense 416 mμ band lies at the wavelength close to that of

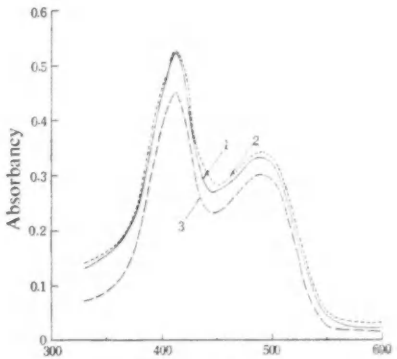


Fig. 4. Absorption spectra of picryl chloride (1.77×10^{-5} mol.) in ethanol (containing 4% water by volume) in the presence of sodium hydroxide (4.16×10^{-2} N) at room temperature.
1 immediately after the preparation,
2 after 2 hr.,
3 after 20 hr.

the maximum for an aqueous solution of a red complex obtained from an acetone solution of picryl chloride in the presence of ammonia water[6].

Absorption Spectra of the Red-Colored Solution in Ethanol.—The orange ethanolic solution of picryl chloride was made by pipetting 1 cc. of an aqueous sodium hydroxide solution into an ethanolic picryl chloride solution and diluting the solution to 25 cc. As indicated in Fig. 4, the orange ethanolic solution shows two absorption maxima at about 412 and 490 mμ close to those of the bands for the orange aqueous solution of picryl chloride. Yellow crystals began to precipitate from the orange ethanolic solution allowed to stand at room temperature for two hours. As shown in Fig. 4, the part of the solution gives the absorption maxima at the same wavelengths.

3) J. Meisenheimer, *Ann.*, **323**, 205, 214, 241 (1902).
4) R. Foster and D. LL. Hammick, *J. Chem. Soc.*, **1954**, 2153; R. Foster, *Nature*, **176**, 746 (1955); **183**, 1042 (1959).
5) J. B. Ainscough and E. F. Caldin, *J. Chem. Soc.*, **1956**, 2528.
6) T. Abe, This Bulletin, **32**, 997 (1959).
7) T. Abe, ibid., **33**, 41 (1960).
8) R. C. Farmer, *J. Chem. Soc.*, **1959**, 3425.
9) R. C. Farmer, ibid., **1959**, 3430, 3433.
10) M. Kimura, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **73**, 1219 (1953); M. Kimura and M. Thoma, ibid., **78**, 1401 (1958).
11) M. Kimura, *Pharm. Bull.* (*Japan*), **3**, 75 (1955).
12) M. Akatsuka, *J. Pharm. Soc. Japan* (*Yakugaku Zasshi*), **80**, 378, 384, 390 (1960).
13) S. Nagakura, S. Oosawa and H. Tsubomura, presented at the Symposium on Electronic States of Molecules, Kyoto, October, 1958.
14) S. Nagakura and S. Oosawa, presented at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1959.
15) S. Nagakura and S. Oosawa, presented at the 13th same Meeting, Tokyo, April, 1960.

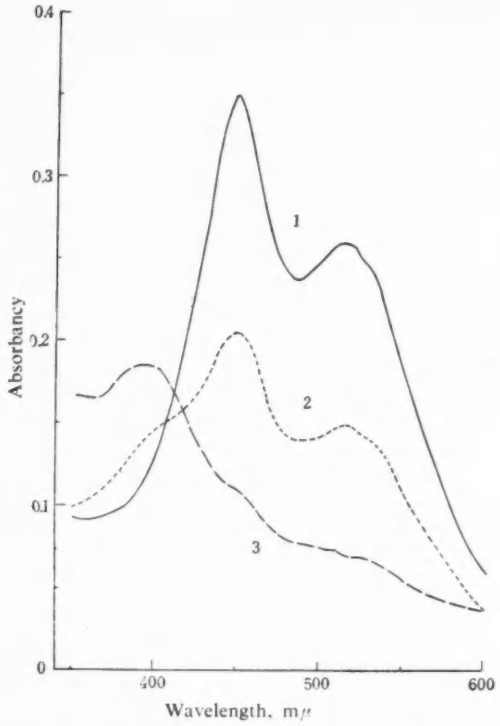


Fig. 5. Absorption spectra of picryl chloride (1.73×10^{-5} mol.) in acetone (containing 4% water by volume) in the presence of sodium hydroxide (4.16×10^{-2} N) at room temperature.
1 immediately after the preparation,
2 after 1 hr.,
3 after 3 hr.

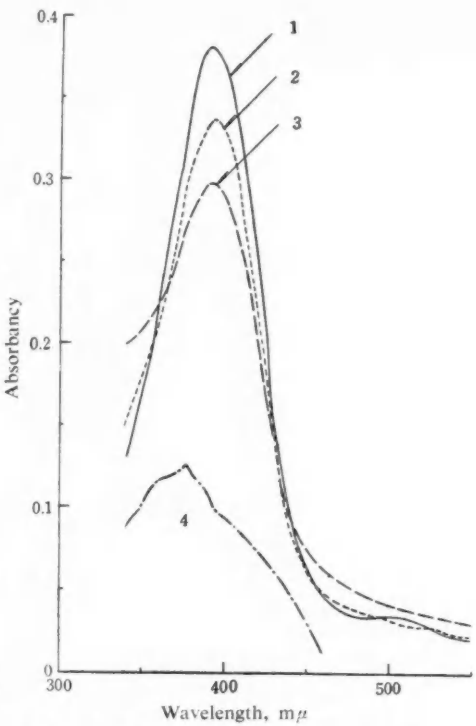


Fig. 6. Absorption spectra of picric acid (1.81×10^{-5} mol.) in acetone (containing 4% water by volume) in the presence of sodium hydroxide (4.16×10^{-2} N) at room temperature.
1 immediately after the preparation,
2 after 1 hr.,
3 after 3 hr.,
4 a solution of picric acid (1.81×10^{-5} mol.) in acetone.

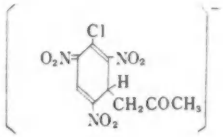
It was reported by Farmer[5] that on treatment of picryl chloride with methanolic potash, Meisenheimer's anion of [Picryl chloride·OCH_3]$^-$ was produced. It was reported by Nagakura and Oosawa[15] that when methoxide ion was added to a methanolic solution of chloro-dinitrobenzene, a red color appeared immediately and soon disappeared, and that chloro-dinitrobenzene was almost completely converted into dinitroanisole. The visible absorption curves in Fig. 4 would be due to Meisenheimer's product II. These absorption curves do not resemble that (showing an intense absorption band at about 425 mμ) of an ethanolic solution of the red complex obtained from the acetone solution of picryl chloride in the presence of ammonia water[6].

Absorption Spectra of the Red-Colored Solution in Acetone.—The reddishorange solution of picryl chloride in acetone was made by pipetting 1 cc. of an aqueous sodium hydroxide solution into an acetone solution of picryl chloride and diluting the solution to 25 cc. As indicated in Fig. 5, the reddishorange solution gives two absorption maximum bands at longer wavelengths of about 450 and 515 mμ, as compared with the orange aqueous solution in Fig. 1 and the orange ethanolic solution in Fig. 4. When allowed to stand, the reddishorange solution gradually changed into a decolorized solution giving a band at about 390 mμ. About three hours after the preparation the reddishorange solution became turbid. The spectra of the solution could not, therefore, be measured after that time.

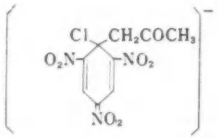
Spectra of a solution of picric acid under the same condition as when the reddishorange solution was prepared, are indicated in Fig. 6. The solution of picric acid showed an intence band at about 390 mμ immediately after the

preparation and also became turbid after about three hours. Absorbancy of the 390 mμ band decreases as the solution is allowed to stand.

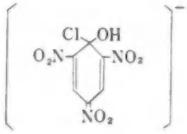
Kimura[11] reported that picryl chloride in a mixture of acetone and methanol (50% by volume) gave an intense 450 mμ band and weak 520~530 mμ ones, and stated that the following four products were responsible for the color, where the product IV was predominant.



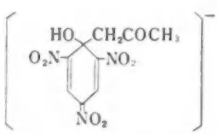
IV



V



VI



VII

The color reactions of trinitrobenzene derivatives with alkalies, however, occur instantaneously at room temperature even in the absence of acetone[1-9,13-15]. The absorption curve 1 in Fig. 5 closely resembles that of 1 in Fig. 1. In addition, the 360 mμ band of the absorption curve 3 in Fig. 5 seems to be due to picric acid produced in comparison with the absorption curves 1-3 in Fig. 6. Accordingly, the curve 1 in Fig. 5 would be due to the product II described above.

The curve (1) in Fig. 5 closely resembles that of a red solution prepared by adding a drop of aqueous sodium hydroxide solution to 1, 3, 5-trinitrobenzene in acetone[16].

Summary

The red solution prepared by adding sodium hydroxide to an aqueous picryl chloride solution containing a small quantity of ethanol, was relatively stable even at room temperature. The red solution showing the two bands at about 416 and 490 mμ, changed into the yellow solution showing the band similar to that of picric acid under the same condition. Accordingly, the 416 and 490 mμ bands may be due to the intermediate of Meisenheimer's type in the process of the substitution reaction of picryl chloride to picric acid.

In the presence of sodium hydroxide, picryl chloride in ethanol as well as in acetone finally gave the absorption bands analogous to that of picric acid in water containing ethanol. The red solutions in ethanol and in acetone, therefore, would be due to the same intermediate.

The author is particularly indebted to Professor Yōkan Nomura for helpful discussions.

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16) T. Abe, This Bulletin, 32, 778 (1959).

Vinyl Polymerization XLVII. Polymerization of Acenaphthylene with Ziegler-Type Catalysts*

By Minoru IMOTO and Isamu SOEMATSU

(Received July 22, 1960)

Recently it was patented by Baxter et al.[1] that indene and acenaphthylene were polymerized in the presence of catalysts containing a titanium, vanadium or molybdenum halide in conjunction with a lithium alkyl, lithium aluminum hydride or lithium aluminum tetraalkyl. Partially crystalline homopolymers as well as copolymers of these polymers with ethylene, propylene or 1-hexadecene were described in the patent examples.

Before the patent was published, a kinetic study on polymerization of acenaphthylene in the presence of catalyst of $Ti(OBu)_4$-$AlEt_3$ or $Ti(OBu)_4$-$LiAlH_4$ was undertaken by the present authors. In this paper, the results obtained are described. In literature, polymerization of vinyl monomer with $Ti(OBu)_4$-$AlEt_3$ is found[2]. However, the system of $Ti(OBu)_4$-$LiAlH_4$ was little investigated.

Experimental

Materials.—Aluminum triethyl was obtained from Mitsui Petroleum Co. It was specified to contain 25.87% Al and 74.10% C_2H_5. The material was used without further purification. The lithium aluminum hydride was of commercial grade. *n*-Butyl titanate was prepared by the descriptions in literature[3]; b. p. 189~189.1°C (16 mmHg), Ti 13.82% (as $Ti(OC_4H_9)_4$, 14.07%). Acenaphthylene was obtained from acenaphthene by its dehyrogenation; m. p. 92~93°C, b. p., 106~107°C/3 mmHg. *n*-Heptane and toluene, pure grade, was purified as usual.

Results

Polymerization of Acenaphthylene with $AlEt_3$-$Ti(OC_4H_9)_4$.—*Procedure.*—Freshly distilled *n*-heptane was added to a 200 ml. three-necked flask with a mercury seal stirrer, an inlet tube for nitrogen and monomer, and a thermometer. The system was flushed with dry nitrogen. A solution of $(BuO)_4Ti$ in heptane and then a solution of $AlEt_3$ in heptane were added under vigorous stirring. Color appeared immediately, varying from light red to deep green. No precipitate was formed. After 10 min. stirring, the monomer solution was introduced dropwise.

The polymerization system was poured into a large excess of methanol and the precipitate was repeatedly purified by reprecipitation from benzene solution with methanol. The polymer thus obtained contained no trace of ash.

Effects of Al/Ti Molar Ratio on Conversion of Monomer and on $[\eta]$ of Polymer.—Keeping

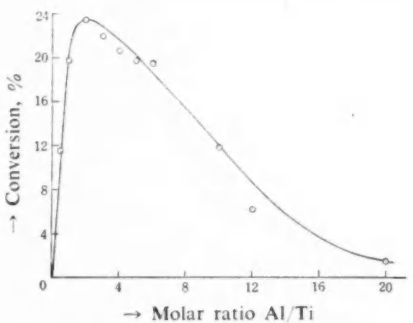

Fig. 1. Conversion of monomer vs. molar ratio of Al/Ti (at 80±0.5°C).

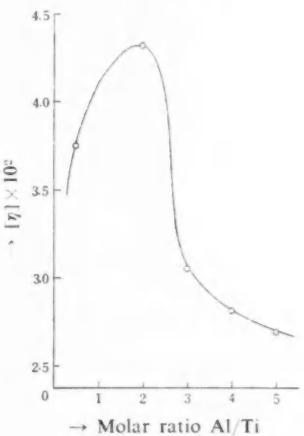

Fig. 2. $[\eta]^{30°}_{\text{Benzene}}$ of polyacenaphthylene vs. molar ratio of Al/Ti.

* XLVI of this series: M. Imoto and M. Matsuda, *High Polymer Chem. (Kobunshi Kagaku)*, **17**, 472 (1960).

1) W. N. Baxter, I. M. Robinson and L. H. Rombach (to duPont) U. S. Pat., 2850488, Spt. 4, 1958.

2) N. G. Gaylord and H. F. Mark, "Linear and Stereoregular Addition Polymers", Interscience Pub., New York (1959), pp. 338, 362.

3) F. Bischoft and H. Adkins, *J. Am. Chem. Soc.*, **46**, 256 (1946).

the quantity of $AlEt_3$ constant at 0.376 g, the quantity of tetrabutyl titanate was varied. 5.00 g. of acenaphthylene was taken. The total volume was 100 ml.

Polymerization was carried out for 10 hr. The results obtained were illustrated in Figs. 1 and 2.

A maximum of conversion appeared at the molar ratio of Al/Ti of 2:1.

Estimation of Activation Energy. — The concentrations of aluminum triethyl and acenaphthylene were 0.376 g. and 5.00 g. in 100 ml. of the reacting solution. The molar ratio of Al/Ti was kept constant at 2:1. The conversions were shown in Fig. 3.

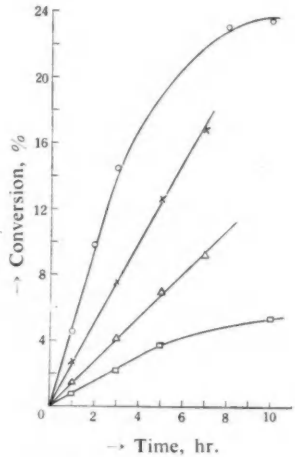

Fig. 3. Conversion of monomer vs. polymerization time.

From the slopes of the conversion curves, the initial rates of polymerisation were computed as Table I.

TABLE I. RATES OF POLYMERIZATION

	R_p(mol./l. sec.)
50±0.05°C	0.723×10^{-6}
60	1.300
70	2.438
80	4.775

From Table I the activation energy for the polymerization of acenaphthylene with $AlEt_3$-$Ti(OC_4H_9)_4$ was computed as 14.3 kcal./mol. (c. f. Fig. 4).

Using collodion film, molecular weight of a polymer was measured by the method of osmotic pressure, as shown in Table II. Intrinsic viscosity was also measured in benzene (c=g./100 ml.).

Even if polyacenaphthylene had the small value of $[\eta]$, its molecular weight measured

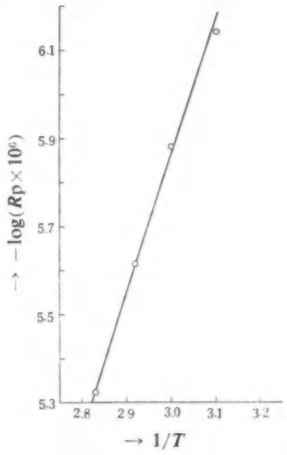

Fig. 4. Estimation of activation energy.

TABLE II.

Polymer	Mol. wt.	$[\eta]^{30°}_{Benzene}$	Literature
Al/Ti=3:1 80°C, 10 hr.	108000	0.035	This paper
BF_3Et_2O (60°C)	125000	0.040	Imoto, Takemoto[4]

by the method of osmotic pressure was very great. As Table II shows, this characteristic figure coincided with the result obtained in the previous paper[4].

Polymerization of Acenaphthylene with $LiAlH_4$-$Ti(OC_4H_9)_4$. — In a tube, 0.0671 g. of $LiAlH_4$, 1.00 g. of acenaphthylene and various quantities of $Ti(OC_4H_9)_4$ in 10 ml. of toluene were sealed. The tubes were heated at 100± 1°C for 2 hr. and then treated as described above. The results were illustrated in Fig. 5.

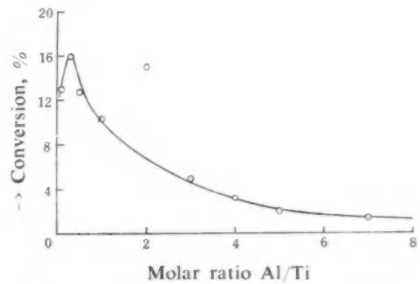

Fig. 5. Conversion of monomer vs. molar ratio of Al/Ti.

The initial rates of polymerization at several reaction temperatures were measured from the conversion curves, as shown in Fig. 6.

4) M. Imoto and K. Takemoto, *J. Polymer Sci.*, **15**, 271 (1955). (The value of $[\eta]$ was not described.)

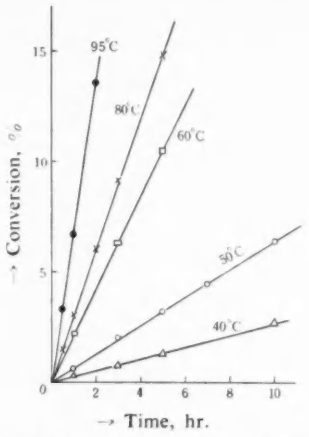

Fig. 6. Conversions of monomer at various temperatures vs. polymerization time.

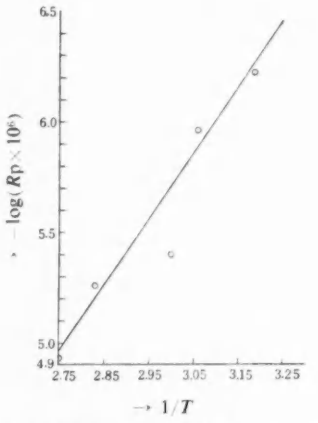

Fig. 7. Estimation of activation energy.

Table III. The initial rates

Temp.	$[Rp]_0$
40±0.05°C	0.603×10^{-6} mol./l. sec.
50	1.15
60	3.99
80	5.55
95	12.2

These observations were made in the condition as follows: $LiAlH_4$ 0.25 g., acenaphthylene 1.00 g., toluene 10 ml. and the molar ratio of Al/Ti 2:1. The computed values of the initial rates are tabulated in Table III.

From the values of $[Rp]_0$ in Table III, the apparent activation energy was estimated at about 13 kcal./mol., as in Fig. 7.

After ten hours polymerization, five kinds of polymers were obtained. As to these polymers, the intrinsic viscosities were measured in benzene at 30±0.1°C and the apparent softening points were observed in sealed tubes. The results were shown in Table IV.

Table IV. $[\eta]$ and softening points

Temp.	$[\eta]$	Soften. pt.
40°C	0.0259	303°C
50	0.0260	305
60	0.0268	302
80	0.0278	309
95	0.0406	305

Polymerization of Styrene and Methyl Methacrylate with $LiAlH_4$-$Ti(OB_iH_9)_4$.—The procedure for polymerization was the same as that described above. 0.0256 g. of $LiAlH_4$ and 0.5 mol. equivalents of $Ti(OB_iH_9)_4$, i.e., the Al/Ti molar ratio 2:1, were used as catalyst. The temperature was 80±1°C and the duration of reaction was 20 hr. The results obtained in toluene were shown in Table V.

Table V.

	Methyl metacrylate g.	Styrene g.	Acenaphthylene, g.	Yield g.
Copolymerization	1.980	—	1.000	1.1235
	—	2.040	1.000	0.1065
Polymerization	1.980	—	—	0.3360
	—	2.040	—	0.6980

Summary

Polymerization of acenaphthylene was studied kinetically in heptane or toluene in the presence of titanium butanate-aluminum triethyl or titanium butanate-lithium aluminum hydride at 40~95°C. Activation energy was computed as 14.3 and about 13 kcal./mol.

Molecular weight of the polymer obtained was 125000, while $[\eta]^{30°}_{\text{Benzene}}$ was only 0.035 (c=g./100 ml.).

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Studies on the Mucilage of the Root of "Tororo-aoi" (Abelmoschus manihot, MEDIC). III. On the Mechanism of the Characteristic Colloidal Nature of the Mucilage

By Saburo INOKAWA

(Received April 28, 1960)

In the previous paper[1] it has been shown that in the freshly purified mucilage there exists a network structure built by a very strong interaction between the mucin molecular chains, and that an irreversible marked loss of the interaction occurs by heat treatment although the change in average molecular weight measured by osmotic pressure is small[2]. The present investigation was undertaken in order to explain the mechanism of the network structure in the fresh mucilage and its breaking by heat treatment. Details are shown as follows.

Experimental

1) Material.—Roots of "*Tororo-aoi*" were stored in 0.5% formalin.

2) Crude Mucilage, Purified Mucin, and Purified Mucilage.—These preparations were similar to those described in the previous paper[3].

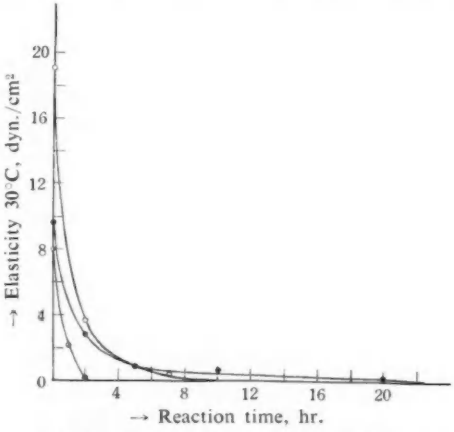

Fig. 1. Effect of addition of H_2O_2, H_2SO_4, or H_2O_2–H_2SO_4 on the elasticity of the purified mucilage.
Concentration of mucilage: 0.53%
○, H_2O_2 (0.12%)
●, H_2SO_4 (9.8%)
◑, H_2O_2–H_2SO_4 (0.06% : 9.8%)

1) S. Inokawa, This Bulletin, 33, 1476 (1960).
2) S. Inokawa, R. Goto and I. Morimoto, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 783 (1960).
3) S. Inokawa, This Bulletin, 33, 1472 (1960).

3) Elasticity and Intrinsic Viscosity.—These determinations were the same as those described in the previous paper[3].

4) Action of Hydrogen Peroxide on the Mucilage.—The elasticity changes (at 15°C) in the purified mucilage in the presence of hydrogen peroxide, sulfuric acid, or the mixture of both, are shown in Fig. 1.

Acetone was added into the mucilage to precipitate the mucin, just when the elasticity could hardly be observed in the above experiments. The mucin thus obtained was washed with acetone, dried up in vacuo and redissolved in water. In the experiment using sulfuric acid, the redissolved mucilage was neutralized with a dilute sodium hydroxide solution. Table I gives the results of measurement of intrinsic viscosity of the redissolved mucilage.

TABLE I. INTRINSIC VISCOSITY OF THE PURIFIED MUCILAGE JUST WHEN THE ELASTICITY COULD HARDLY BE OBSERVED BY ADDITION OF HYDROGEN PEROXIDE, SULFURIC ACID, OR BOTH

Treatment by	Intrinsic viscosity l./g.				Mean value l./g.
H_2O_2	1.7	1.2	1.8	1.6	1.6
H_2SO_4	0.47	0.55	0.58	0.50	0.53
H_2O_2–H_2SO_4	1.8	1.7	1.4	1.7	1.7
Heating at 80°C for 2 hr.	1.5	1.6	1.4	1.4	1.5

The intrinsic viscosity of the mucilage treated with hydrogen peroxide or hydrogen peroxide-sulfuric acid is about the same as that of the heated mucilage. However, that of the mucilage treated with sulfuric acid is 0.52, and is considerably smaller than the above-mentioned values.

5) Effect of Oxygen in the Air upon the Mucilage and the Mucin.—a) The purified mucins, one in nitrogen atmosphere and the other in the air, were

TABLE II. EFFECT OF OXYGEN UPON THE INTRINSIC VISCOSITY LOSS OF THE PURIFIED MUCIN BY HEAT TREATMENT

Heated in	Intrinsic viscosity, l./g.	
	Before heating	After heating at 80°C for 120 min.
N_2 atmosphere	2.86	2.77
Air	2.86	1.83

TABLE III. EFFECT OF OXYGEN UPON THE INTRINSIC VISCOSITY LOSS OF THE PURIFIED MUCILAGE BY HEAT TREATMENT

Condition	Method	Intrinsic viscosity, l./g.		
		Before heating	After heating 80°C, 90 min.	After heating 80°C, 150 min.
Oxygen-free mucilage	High vacuum	2.64	2.23	2.10
	N_2-blowing	2.55	2.20	2.08
Air-containing mucilage		2.80	1.47	1.38

heated at 80°C for 120 min. by the high vacuum method described in the previous paper[4]. Both the heated mucins were dissolved in water and the viscosity was measured. As shown in Table II the intrinsic viscosity of the mucin heated in nitrogen atmosphere does not decrease practically. b) The purified oxygen-free mucilage prepared by the high vacuum method[4] was heated at 80°C and the intrinsic viscosity was measured. As shown in Table III the intrinsic viscosity loss of the purified oxygen-free mucilarge by heating is much smaller than that of the usual air-containing mucilage.

For the purpose of obtaining oxygen-free mucilage more simply, oxygen-free nitrogen[5] was blown for 10 hr. into the purified mucilage in the glass tube shown in Fig. 2, and then the glass tube was sealed off first at A and next at B. The viscosity loss of the obtained oxygen-free mucilage by heating was similar to that of oxygen-free mucilage prepared by the high vacuum method as shown in Table III. Then, the effect of oxygen upon the elasticity loss of the purified mucilage by heating was examined

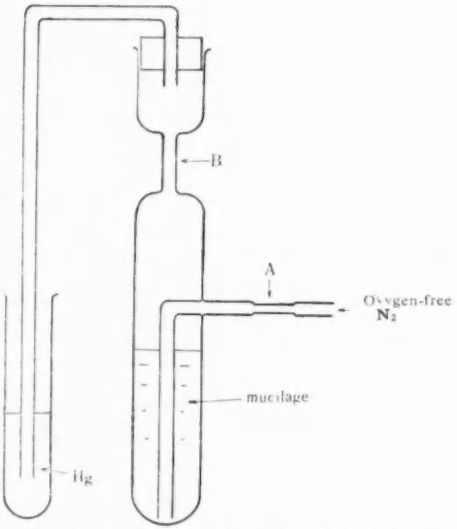

Fig. 2. Apparatus for the blowing method.

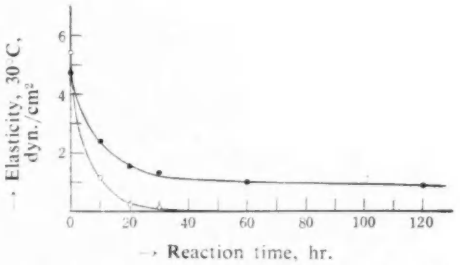

Fig. 3. Effect of oxygen on the elasticity fall of the purified mucilage by heating.
Concentration of mucilage: 0.31%.
○, air-containing mucilage
●, oxygen-free mucilage

by this nitrogen-blowing method. The elasticity loss of nitrogen-blowing mucilage by heating as shown in Fig. 3 is much smaller than that of the air-containing mucilage.

6) Muddy Matter Produced by Heating.—It has been reported[1], from the observation of sedimentation diagrams of the heated purified mucilage in an ultracentrifuge that there was something which sedimented rapidly in the initial few minutes. A precipitate[6] (ca. 1.1 wt. % of mucin), which was dispersed easily by irradiation of ultrasonic wave, was obtained from the purified mucilage heated at 95°C for 16 hr. The dispersed precipitate was mounted on a specimen holder for electron microscopy with a formvar supporting-film and dried.

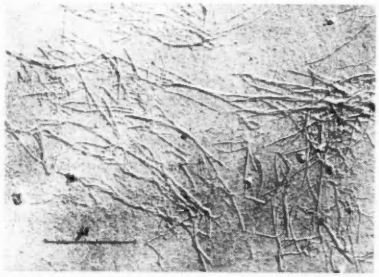

Fig. 4. Electron micrograph of the precipitate produced by heating the purified mucilage. (dispersed by ultrasonic wave) (Cr-shadowing)

4) S. Inokawa, R. Goto and E. Fujimoto, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 678 (1960).

5) By blowing of carbon dioxide instead of nitrogen, similar results were obtained.

6) This precipitate did not show reactions of starch.

After chromium-shadowing the specimen was observed by an electron microscope of the type Akashi TRS-50 B, showing a fine fiber-like picture as shown in Fig. 4. The nitrogen content of the precipitate was 1.9%. After hydrolysis of the precipitate in 2 N hydrochloric acid at 100°C for 22 hr. in a sealed tube, the hydrolyzed solution was diluted with water, filtered, passed through a cation-exchange resin Amberlite IR-112, evaporated, and dried, in vacuo. From the residue only glucose was detected by paper chromatography using the solvent system: ethyl acetate: pyridine: water (12 : 5 : 4).

7) **Effect of Potassium Thiocyanate, Sodium Lauryl Sulfate, Guanidine Hydrochloride, and Dichloro acetic Acid on the Elasticity of the Purified Mucilage.**—Fig. 5 shows the elasticity curves plotted against concentrations of four sorts of reagents. It is observed that the elasticity is practically uninfluenced by the addition of these reagents[7].

8) **Periodate Oxidation of the Mucilage.**—The mucilage (0.448 g.) was dissolved in water (in 500 ml. bottle), and sodium periodate solution (0.2 M, 10 ml.) was added, followed by water to the requisite volume. Formic acid was yielded, and uptake of periodate of the solution followed. The results are tabulated in Table IV. It is clear that 1 M of formic acid was produced by consuming 2 M of periodate.

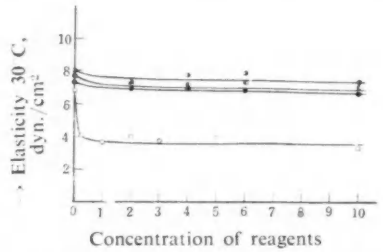

Fig. 5. Effect of addition of potassium thiocyanate sodium lauryl sulfate, guanidine hydrochloride, and dichloroacetic acid on the elasticity of the purified mucilage.
Concentration of mucilage: 0.36%.
●, potassium thiocyanate
◐, sodium lauryl sulfate
◑, guanidine hydrochloride
○, dichloroacetic acid

TABLE IV. PERIODATE OXIDATION OF THE MUCILAGE AT 15°C[8]

Time, hr.	Formic acid produced mol./G mol.[9]	Consumed IO_4^- mol./G mol.
0	0	0
10	0.72	1.21
24	1.09	1.64
52	1.19	2.02
75	1.23	2.07
125	1.24	2.14

7) It seems to be reasonable that a little loss in elasticity by the addition of dichloroacetic acid was caused by a change of pH in the mucilage because the elasticity loss was identical with the case in which acetic acid or oxalic acid was added.

8) P. F. Fleury and J. Lange, *J. pharm. Chim.*, [8], **17**, 107, 196 (1933).

9) The value of G mol. was assumed to be 161, which is the mean value of molecular weight of rhamnose and galacturonic acid.

Discussion

It is said that the mucin of "*Tororo-aoi*" is a polysaccharide consisting of rhamnose and galacturonic acid linked in straight chains[10] and the molecular weight is very high, that is, the value is 150000~200000[2]. The relative amounts of the components vary, depending on the source. However, it is shown from the results of periodate-oxidation (experiment 8) that the mucin molecule has branched chains. Thus, it seems to be plausible that the mucin molecule is a long chain polysaccharide with many short branched chains. Also, it has been shown that in the fresh purified mucilage there exists a network structure like a gel[1]. Considering that the elasticity is little changed by the electrolysis[3] or the addition of sodium chloride[2], the network structure may not be built by intermolecular ionic bonds of the mucin. Moreover, the elasticity is little influenced by the addition of potassium thiocyanate, sodium lauryl sulfate, guanidine hydrochloride, and dichloroacetic acid (experiment 7). Therefore the network structure may not be built by hydrogen bonds between mucin molecules. Also, the agitation of mucilage causes an irreversible diminution of the elasticity[3]. From the consideration of these experimental results, it seems to be most reasonable to suppose that the network structure is built by interlocking or entanglement of mucin molecules.

By heating, the elasticity of the purified mucilage diminishes and at the same time muddy matters consisting of fibrous glucosans and proteins were produced (experiment 6) but the molecular weight change is slight[2]. These experimental results mentioned above would lead to the conclusion that the mucin molecules are entangled between short branched chains of the mucin molecules, fibrous glucosans and proteins. On heating, the entanglement is broken by oxidation (experiment 5).

Summary

1) The colloidal characteristics of the mucilage from "*Tororo-aoi*" such as the elasticity, spinnability, and so on are caused by the network built by interlocking between short branched chains of the mucin molecules, fibrous glucosans and proteins.

10) S. Machida and N. Uchino, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **74**, 183 (1953).

2) The remarkable change of the colloidal nature by heating is caused by breaking down the interlocking by oxidation.

Finally the writer wishes to express his hearty thanks to Professor R. Goto, Kyoto University, for his invaluable advice and encouragement throughout this work. He is also indebted to Professor E. Suito and Dr. K. Takiyama of Kyoto University for their help in the preparation of the electron micrographs, and further to Mr. A. Sera, Mr. A Takatsuki, Mr. I. Morimoto and Mr. E. Fujimoto for their kind co-operation in this research. It is a pleasure to thank Koshin Kogyo Co. for the generous supply of roots of "*Tororo-aoi*".

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Hydrogenation and Hydrogenolysis. V[1]. *Rhodium-Platinum Oxide as a Catalyst for the Hydrogenation of Organic Compounds*[2]

By Shigeo NISHIMURA

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In previous papers[1,2], it was reported that rhodium-platinum oxide, prepared by fusion of the mixture of rhodium chloride and chloroplatinic acid or ammonium chloroplatinate in a ratio of 3 : 1 by the weights of the metals with sodium nitrate exactly in the same way as in the preparation of Adams platinum oxide, can be reduced with hydrogen to the metal form under ordinary conditions and also that the resulting rhodium-platinum black is an excellent catalyst retaining the nature of pure rhodium catalysts and is substantially superior to Adams platinum oxide both in activity and in selectivity in the hydrogenation of various aromatic compounds. The present paper describes the use of the rhodium-platinum oxide as a catalyst and also the comparisons with platinum oxide and with palladous oxide in the hydrogenation of various organic compounds under ordinary conditions.

Experimental

Materials. — The oxide catalysts were prepared according to the procedures described in the preceding paper[1]. Glacial acetic acid of Wakō Pure Chemical Industries G. R. grade was used without further purification. Commercial 95% ethanol was used after distillation. All the substrates were carefully purified before use by recrystallization or by distillation.

Hydrogenation.—Hydrogenation was carried out under atmospheric pressure and at room temperature (24~26°C). After the oxide was reduced to metal, the substance was added with a small amount of solvent, and the mixture was shaken with hydrogen at about 350~400 oscillations per minute.

Results and Discussion

Catalytic Reduction, where the C–O Linkage is Liable to Hydrogenolysis. — As already reported in previous papers[1,2], the compounds, which have C–O linkages susceptible to hydrogenolysis, are less hydrogenolyzed and much more rapidly hydrogenated in acetic acid with rhodium-platinum oxide than with platinum oxide[3]. Further results are shown in Tables I and II, and also the hydrogenation of acetophenone in Table III and furfuryl alcohol in Table IV. If less hydrogenolysis is desired, it is preferable to use ethanol with a small amount of acetic acid as the solvent, as shown in the hydrogenation of benzyl methyl ether[4]. Benzyl acetate is almost completely hydrogenolyzed even under these conditions. The addition of a slight amount of hydrochloric acid increases the hydrogenolysis as shown in the hydrogenation of hydroquinone with platinum oxide[5].

Aliphatic and alicyclic ketones are also less hydrogenolyzed and much more rapidly hydrogenated with rhodium-platinum oxide than with platinum oxide in acetic acid (Table II).

1) Part IV of this series: S. Nishimura, T. Onoda and A. Nakamura, This Bulletin, 33, 1356 (1960).
2) Cf. Part III of this series: S. Nishimura, ibid., 33, 566 (1960).
3) Cf. H. A. Smith and R. G. Thompson, "Advances in Catalysis", Vol. 9, Academic Press Inc., New York (1957), p. 727.
4) Cf. S. Nishimura, This Bulletin, 32, 1155 (1959).
5) For the effect of the solvent on the hydrogenation and hydrogenolysis, see, for instance, Ref. 1.

TABLE I. CATALYTIC REDUCTION OF AROMATIC COMPOUNDS WHERE THE C–O LINKAGE IS LIABLE TO HYDROGENOLYSIS

Compound, g.	Solvent, ml.	Catalyst, g.	Hydrogen uptake mol./mol.	Time for hydrogenation min.
Benzyl methyl ether, 0.611	EtOH, 20	Rh-Pt oxide, 0.10	S.*	
〃	〃	Pt oxide, 0.20	S.*	
〃	EtOH, 20 + AcOH, 0.02	Rh-Pt oxide, 0.10	3.13	120
〃	〃	Pt oxide, 0.20	3.13	240
〃	AcOH, 20	Rh-Pt oxide, 0.05	3.48	80
〃	〃	Pt oxide, 0.05	3.89	130
Benzyl alcohol, 0.541	〃	Rh-Pt oxide, 0.05	I.**	
〃	〃	Pt oxide, 0.05	3.95	120
Benzyl acetate, 0.751	〃	Rh-Pt oxide, 0.05	3.94	14
〃	〃	Pt oxide, 0.05	3.99	60
Hydroquinone, 1.101	AcOH, 30	Rh-Pt oxide, 0.05	3.25	40
〃	〃	Pt oxide, 0.05	4.01	110
〃	AcOH, 30 + 3 N HCl, 0.1	〃	4.59	120
Methyl salicylate, 0.761	AcOH, 20	Rh-Pt oxide, 0.10	3.13	65
〃	〃	Pt oxide, 0.10	3.26	200
α-Naphthol, 0.721	〃	Rh-Pt oxide, 0.10	5.17	270
〃	〃	Pt oxide, 0.10	5.16	300
β-Naphthol, 0.721	〃	Rh-Pt oxide, 0.10	5.21	85
〃	〃	Pt oxide, 0.10	5.37	275

* Slow reduction.

** Incomplete reduction because of the decreasing rate.

TABLE II. CATALYTIC REDUCTION OF ALIPHATIC AND ALICYCLIC KETONES

Compound, g.	Solvent, ml.	Catalyst, g.	Hydrogen uptake mol./mol.	Time for hydrogenation min.
Diethyl ketone, 0.861	AcOH, 20	Rh-Pt oxide, 0.05	1.01	140
〃	〃	Pt oxide, 〃	1.01	150
Cyclohexanone, 0.981	〃	Rh-Pt oxide, 〃	1.03	7
〃	EtOH, 20	Pt oxide, 〃	1.00	80
〃	AcOH, 20	〃 〃	1.27	30
〃	AcOH, 20 + 3 N HCl, 0.1	〃 〃	1.31	24
Cyclopentanone, 0.841	AcOH, 20	Rh-Pt oxide, 〃	1.08	40
〃	〃	Pt oxide, 〃	1.56	200
Ethyl acetoacetate, 1.302	〃	Rh-Pt oxide, 〃	1.11	15
〃	〃	Pt oxide, 〃	1.56	300

In neutral ethanolic solution these ketones are hydrogenated quantitatively with platinum oxide to the corresponding alcohols with the absorption of just one mole of hydrogen, and the addition of hydrochloric acid increases hydrogenolysis, though only to a small extent, as shown in the hydrogenation of cyclohexanone. As is well known, palladous oxide is practically ineffective for the hydrogenation of these ketones. Details of the hydrogenation and hydrogenolysis of aliphatic and alicyclic ketones will be published later.

Catalytic Reduction of Acetophenone (Table III).—Acetophenone is reduced with rhodium-platinum oxide to cyclohexylmethylcarbinol quantitatively in ethanol and almost quantitatively in acetic acid. The hydrogenation is especially rapid in the latter solvent accompanied only by a slight hydrogenolysis (6%). With platinum oxide, in ethanol as the solvent, one mole of hydrogen is absorbed rather rapidly and further reduction occurs only very slowly, and in acetic acid as the solvent, as much as 84% is hydrogenolyzed to give ethylcyclohexane as indicated by the hydrogen uptake. Both platinum oxide and palladous oxide show the greatest activity for the reduction to ethylbenzene in the presence of acetic acid with

TABLE III. CATALYTIC REDUCTION OF ACETOPHENONE

Acetophenone g.	Solvent, ml.	Catalyst, g.	Hydrogen uptake mol./mol.	Time for hydrogenation min.
0.601	EtOH, 20	Rh-Pt oxide, 0.05	3.98	8/1 mol. 130/4 mol.
〃	〃	Pt oxide, 〃	S. after 1 mol.	25/1 mol.
〃	AcOH, 20	Rh-Pt oxide, 〃	4.06	24
〃	〃	Pt oxide, 〃	4.84	110
〃	AcOH, 20+ 3 N HCl, 0.1	Rh-Pt oxide, 〃	S.	
〃	〃	Pt oxide, 〃	5.03	16/2 mol. 120/5 mol.
1.201	EtOH, 20	Pd oxide, 〃	1.98	20/1 mol. 200/2 mol.
〃	AcOH, 20	〃 〃	1.98	15/1 mol. 60/2 mol.
〃	AcOH, 20+ 3 N HCl, 0.1	〃 〃	1.99	14/1 mol. 30/2 mol.

Reduction on a preparative scale

Acetophenone g.	Solvent ml.	Catalyst, g.	Reactivation with air	Hydrogen uptake mol./mol.	Time hr.	Time min.	Product
12.01	AcOH, 50	Rh-Pt oxide, 0.2	twice	4.06	3	30	Cyclohexylmethylcarbinol, 80%. B.p. 91°C/22 mmHg; n_D^{20} 1.4652

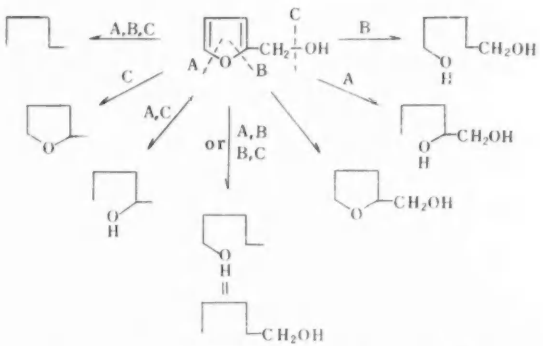

Fig. 1. Catalytic reduction of furfuryl alcohol.

added hydrochloric acid, while the reduction proceeds only very slowly with rhodium-platinum oxide in the same medium. As is well known, palladium is a catalyst preferred for the selective reduction of the side chain because of its low activity for the hydrogenation of the benzene nucleus. Like platinum and palladium catalysts, deactivated rhodium-platinum is also reactivated by shaking with air, and this process is very effective in the hydrogenation of a larger amount of a substrate.

Catalytic Reduction of Furfuryl Alcohol (Table IV).—The complete hydrogenation of furfuryl alcohol under mild conditions is generally expected to give the seven compounds as the result of various competitive reactions between the hydrogenation of the double bonds and the hydrogenolysis of the three C–O linkages indicated by A, B and C, as illustrated in Fig. 1. The kinds and amounts of the products largely depend on the nature of the catalyst and the solvent used. Both rhodium-platinum oxide and palladous oxide give tetrahydrofurfuryl alcohol quantitatively in acetic acid as well as in ethanol with the absorption of two moles of hydrogen. The reduction proceeds most rapidly with rhodium-platinum oxide in acetic acid. With platinum oxide the reduction could not be completed in ethanol because of the decreasing rate of the hydrogenation. But in acetic acid the reduction proceeds smoothly to completion

TABLE IV. CATALYTIC REDUCTION OF FURFURYL ALCOHOL

Furfuryl alcohol g.	Solvent, ml.	Catalyst, g.	Hydrogen uptake mol./mol.	Time for hydrogenation min.
0.981	EtOH, 20	Rh-Pt oxide, 0.05	1.96	42
〃	〃	Pt oxide, 〃	I.	
〃	〃	Pd oxide, 〃	1.95	105
〃	AcCH, 20	Rh-Pt oxide, 〃	1.97	28
〃	〃	Pt oxide, 〃	2.86	115
〃	〃	Pd oxide, 〃	1.96	45
〃	EtOH, 20+ 3 N HCl, 0.1	Pt oxide, 〃	3.11	120
〃	AcOH, 20+ 3 N HCl, 0.1	〃 〃	3.38	85
〃	〃	Pd oxide, 〃	S. after 2.03 mol.	35/2 mol.

TABLE V. PRODUCTS OF CATALYTIC REDUCTION OF FURFURYL ALCOHOL WITH PLATINUM OXIDE IN ETHANOL (OR TETRAHYDROFURFURYL ALCOHOL) WITH HYDROCHLORIC ACID

Product	Yield, %	B. p., °C	n_D^{20}
Pentane*	0.8	35	
2-Methyltetrahydrofuran*	14.8	75～84	1.4031
2-Pentanol	5.5	120～123	1.4047
1-Pentanol	11.6	137～139	1.4096
Tetrahydrofurfuryl alcohol	20.6	173～177	1.4505
1,2-Pentanediol	13.3	110～113/21 mmHg	1.4402
1,5-Pentanediol	3.3	138～142/21 mmHg	1.4499

* These compounds were isolated with the use of tetrahydrofurfuryl alcohol as the solvent.

with an extensive hydrogenolysis as indicated by the absorption of 2.86 mol. of hydrogen[6]. On the other hand, in the presence of hydrochloric acid and ethanol (or tetrahydrofurfuryl alcohol), all the seven compounds were obtained with absorption of 3.11 mol. of hydrogen as shown in Table V[7]. The portion of hydrogenolysis increases further in the presence of acetic acid and hydrochloric acid. With palladous oxide, even in the presence of hydrochloric acid, no hydrogenolysis occurs before the saturation of the double bonds.

Catalytic Reductions of Other Aromatic and Heterocyclic Compounds (Table VI).—Rhodium-platinum oxide is as effective for the hydrogenation of pyridine and quinoline as for aromatic compounds, and substantially more active than platinum oxide also in these hydrogenations. The rhodium-platinum catalyst is also the most active of the three oxides in the hydrogenation of the double bond of the side chain as shown in the hydrogenation of ethyl cinnamate (Table VI) and cinnamyl alcohol (Ref. 1). Palladous oxide is more active in these hydrogenations than platinum oxide.

Catalytic Reduction of Nitrobenzene (Table VII).—Rhodium-platinum oxide is also the most active catalyst in the hydrogenation of nitrobenzene to aniline. Contrary to platinum oxide and palladous oxide, rhodium-platinum oxide is more active in acetic acid than in ethanol. The subsequent hydrogenation of the benzene nucleus proceeds rather slowly both with rhodium-platinum oxide and with platinum oxide in acetic acid. Palladous oxide is almost entirely ineffective for the hydrogenation.

The present results with those reported previously show that the rhodium-platinum (3:1) oxide is a substantially more active catalyst than platinum oxide and palladous oxide in the hydrogenation of various organic compounds under ordinary conditions[8], and especially effective where it is desired to avoid hydrogenolysis. Decrease of the platinum in the rhodium-platinum oxide depresses the hydrogenolysis further, but only to a small extent. On

6) H. A. Smith and J. F. Fuzek, *J. Am. Chem. Soc.*, **71**, 415 (1949), report that 1,2-pentanediol was obtained almost quantitatively under similar conditions.

7) W. E. Kaufmann and R. Adams, *J. Am. Chem. Soc.*, **45**, 3029 (1923), reported that 1-pentanol, 1,2- and 1,5-pentanediols and tetrahydrofurfuryl alcohol were obtained with platinum oxide in the presence of ethanol and a small amount of ferrous chloride with the absorption of 2.5 mol. of hydrogen. Their results show that only the C-O linkages A and B were hydrogenolyzed under these conditions.

8) The metal content of rhodium-platinum (3:1) oxide is only 65% of its weight. The value is considerably smaller than those of platinum oxide (80%) and palladous oxide (87%). Therefore, the activity of the rhodium-platinum oxide is much greater when compared in a unit weight of the metal.

TABLE VI. CATALYTIC REDUCTIONS OF OTHER AROMATIC AND HETEROCYCLIC COMPOUNDS

Compound, g.	Solvent, ml.	Catalyst, g.	Hydrogen uptake mol./mol.	Time for hydrogenation min.
Toluene, 0.921	AcOH, 20	Rh-Pt oxide, 0.05	3.02	28
〃	〃	Pt oxide, 〃	3.01	110
Biphenyl, 0.771	〃	Rh-Pt oxide, 〃	5.99	180
〃	〃	Pt oxide, 〃	6.01	440
Ethyl cinnamate, 1.762	〃	Rh-Pt oxide, 〃	4.06	6/1 mol. 65/4 mol.
〃	〃	Pt oxide, 〃	4.01	30/1 mol. 250/4 mol.
〃	〃	Pd oxide, 〃	1.02	10/1 mol.
Pyridine, 0.791	〃	Rh-Pt oxide, 〃	3.01	28
〃	〃	Pt oxide, 〃	3.01	170
Quinoline, 0.646	〃	Rh-Pt oxide, 〃	5.02	80
〃	〃	Pt oxide, 〃	4.98	200

Reduction on a preparative scale

Toluene g.	Solvent ml.	Catalyst, g.	Reactivation with air	Hydrogen uptake mol./mol.	Time hr.	Time min.	Product
9.21	AcOH, 50	Rh-Pt oxide, 0.2	once	2.99	1	50	Methylcyclohexane, 79%. B. p. 100~101°C

TABLE VII. CATALYTIC REDUCTION OF NITROBENZENE

Nitrobenzene g.	Solvent, ml.	Catalyst, g.	Hydrogen uptake mol./mol.	Time for hydrogenation min.
1.231	EtOH, 20	Rh-Pt oxide, 0.05	S. after 3 mol.	10/3 mol.
〃	〃	Pt oxide, 〃	〃	14/3 mol.
〃	〃	Pd oxide, 〃	3.00	24
〃	AcOH, 20	Rh-Pt oxide, 〃	6.00	6/3 mol. 190/6 mol.
〃	〃	Pt oxide, 〃	5.97	20/3 mol. 230/6 mol.
〃	〃	Pd oxide, 〃	3.00	40

the other hand, the decrease of platinum causes the following disadvantages: (a) It takes a longer time for the reduction of the oxide to the metal. (b) The recovery of the catalyst becomes more difficult, because the residue insoluble in aqua regia increases with the decrease of the platinum[9]. For the reasons mentioned above, the present author chooses the proportion 3:1 of the two metals in the rhodium-platinum oxide as satisfactory for most hydrogenations and convenient for practical use. The fact that the rhodium-platinum oxide is not identical with a mere mixture of rhodium oxide and platinum oxide, the former being reduced with hydrogen much more rapidly and uniformly than the latter, was further confirmed by an X-ray diffraction of these oxides. The peak of rhodium oxide at $2\theta=28°$ (Cu-K_α radiation) disappers completely and most of other peaks of the oxide are greatly deformed in the pattern of rhodium-platinum (3:1) oxide, while the peak of rhodium oxide at 28° and the peak of platinum oxide at 33.3° are clearly detected in the pattern of a mechanical mixture of rhodium oxide and platinum oxide in a ratio of 3:1 by the weights of the metals.

The author wishes to express his hearty thanks to Professor Yoshiyuki Urushibara for his valuable suggestions and encouragement. The author is also indebted to Dr. Hiroshi Takahashi for the measurement of the X-ray diffraction and to the Ministry of Education for a Grant-in-Aid for Scientific Research.

9) This insoluble residue can be dissolved, e. g., by heating with hydrobromic acid and bromine at 100°C in a sealed tube ("Gmelins Handbuch der Anorganischen Chemie", Vol. 64, Verlag Chemie, G. m. b. H., Berlin (1938), p. 43.).

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Molecular Orbital Theory of Reactivity in Non-Alternant Hydrocarbons

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In the past decades there have been proposed not a few theoretical indexes for explaining chemical reactivity of a conjugated system. These are such as π-electron density[1], self-polarizability[2], free valence[3], localization energy[4], Dewar's approximate localization energy[5], frontier electron density[6], superdelocalizability[7], and so forth[8,9]. These quantities were derived from entirely different physical grounds. Nevertheless, predictions of the position of chemical attack by these quantities agreed well with known experimental results. This remarkable fact has attracted the attention of theoretical chemists, and several authors have attempted to interrelate these quantities[3,5,10-12]. The mathematical relations underlying these quantities in alternant hydrocarbons and hetero-alternant molecules have been clarified by the present authors[13] and Baba[14]. That is, as far as some conditions are satisfied, theoretical indexes in static, localization, and frontier electron methods were found to be entirely parallel. If this were so, good coincidence between the indexes and experiments does not always mean that each one of these indexes is the true reflection of the process of reaction. Rather, a possibility might exist that some of them are not qualified as the "good" index in the most general sense and the coincidence of such quantities with experimental facts may due mainly to the existing mathematical relations.

In this connection we should compare the theoretical prediction of an index with experimental data with regard to the compounds in which no such mathematical interrelation as found in alternant hydrocarbons exists. This will serve as testing the availability of theories and finding out the theory closest to the true mechanism of reaction. For this purpose the most suitable material may be non-alternant hydrocarbons in which less intimate relations than in alternant molecules are expected between these theoretical indexes.

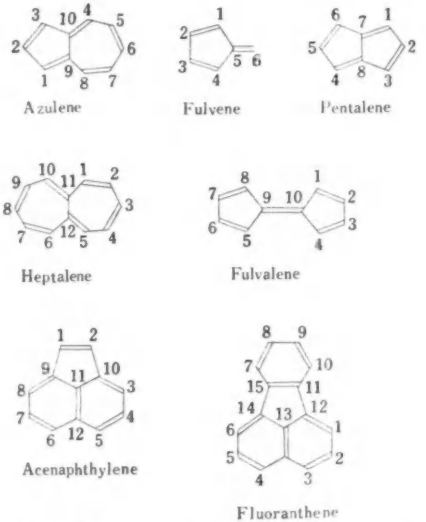


Fig. 1. Structure and numbering of non-alternant hydrocarbons.

In the present paper frontier electron density and superdelocalizability for several non-alternant hydrocarbons were calculated. The structure and numbering of these hydrocarbons are shown in Fig. 1. The calculated values of frontier electron density and superdelocalizability were compared with known experimental results, together with other theoretical indexes.

Results and Discussion

Theoretical indexes of non-alternant hydrocarbons were compared with experiments for three cases of reactions, that is, for electrophilic, radical and nucleophilic reactions, respectively.

1) G. W. Wheland and L. Pauling, *J. Chem. Phys.*, **1**, 606 (1933), etc.
2) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, **A191**, 39 (1947); **A192**, 16 (1947).
3) F. H. Burkitt, C. A. Coulson and H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **47**, 553 (1951).
4) G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1940).
5) M. J. S. Dewar, ibid., **74**, 3341 (1952).
6) K. Fukui, T. Yonezawa and H. Shingu, *J. Chem. Phys.*, **20**, 722 (1952); K. Fukui, T. Yonezawa, C. Nagata and H. Shingu, ibid., **22**, 1433 (1954).
7) K. Fukui, T. Yonezawa and C. Nagata, ibid., **27**, 1247 (1957).
8) S. Nagakura and J. Tanaka, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **75**, 993 (1954).
9) T. Nakajima, *J. Chem. Phys.*, **25**, 587 (1955).
10) H. H. Greenwood, *Trans. Faraday Soc.*, **48**, 585 (1952); *J. Chem. Phys.*, **20**, 1333 (1952).
11) B. Pullman, *Cahier d. phys.*, **48**, 42 (1954).
12) R. D. Brown, *Quart. Rev. Chem. Soc.*, **6**, No. 1, 63 (1952).
13) K. Fukui, T. Yonezawa and C. Nagata, *J. Chem. Phys.*, **26**, 831 (1957).
14) H. Baba, This Bulletin, **30**, 147, 154 (1957).

Reaction with an Electrophilic Reagent.—In Table I, the values of localization energy, frontier electron density and superdelocalizability for an electrophilic attack and the value of π-electron density were listed and compared with known experimental results. The values corresponding to the predicted position of attack are specified by italic letters. Experiments were once carried out for azulene, acenaphthylene and fluoranthene. As is seen in Table I, all indexes predict the same position as the most reactive for azulene and for acenaphthylene in accordance with experiments[15,16]. For fluoranthene, however, the situation is different. That is, the experiments showed that the bromination reaction occurred at two positions giving 3,8-dibromo fluoranthene[17,18]. The prediction of frontier

TABLE I. LOCALIZATION ENERGY ($L_r^{(E)}$), FRONTIER ELECTRON DENSITY ($f_r^{(E)}$), AND SUPERDELOCALIZABILITY ($S_r^{(E)}$) FOR ELECTROPHILIC ATTACK AND π-ELECTRON DENSITY (Q_r) IN COMPARISON WITH EXPERIMENTS

Compounds (Experimental position of attack)	Position	$f_r^{(E)}$	$S_r^{(E)}$	$L_r^{(E)}$	Q_r
Azulene	1	*0.590*	*1.760*	*1.352*	*1.173*
(1)	2	0.000	1.017	1.728	1.047
	4	0.051	0.706	1.808	0.855
	5	0.225	1.035	1.659	0.986
	6	0.000	0.680	1.959	0.870
	9	0.134	0.951	—	1.027
Fulvene	1	*0.724*	*1.850*	*2.002*	*1.092*
	2	0.276	1.399	2.238	1.073
	5	0.000	0.894	2.994	1.047
	6	0.000	0.675	2.230	0.623
Pentalene	1	0.029	0.467	2.380	0.815
	2	*0.526*	*1.365*	*2.027*	*1.173*
	7	0.416	1.241	—	1.198
Heptalene	1	*0.333*	*0.816*[a]	*1.660*	*1.125*
	2	0.000	0.000	2.032	0.882
	3	*0.333*	*0.816*	1.715	1.119
	11	0.000	0.000	—	0.867
Fulvalene	1	*0.361*	*1.351*	*1.987*	*1.097*
	2	0.138	0.966	2.236	0.976
	9	0.000	0.569	—	0.853
Acenaphthylene	1	*0.529*	*1.564*	*2.124*	*1.066*
(1)	3	0.089	0.922	2.525	0.909
	4	0.005	1.026	2.513	1.008
	5	0.119	1.032	2.417	0.926
	10	0.069	1.041	—	1.044
	11	0.356	1.355	—	1.095
	12	0.021	0.819	—	0.998
Fluoranthene	1	0.083	0.779	1.77	0.947
(3 and 8)	2	0.057	0.820	1.82	*1.005*
	3	*0.185*	*1.289*	*1.67*	0.958
	7	0.150	1.078	*1.71*	0.997
	8	*0.152*	*1.105*	1.76	*1.008*

a) Calculated according to the formula of Eq. 27 of Ref. 7.

TABLE II. FRONTIER ELECTRON DENSITY ($f_r^{(R)}$), SUPERDELOCALIZABILITY ($S_r^{(R)}$) AND LOCALIZATION ENERGY ($L_r^{(R)}$) FOR RADICAL ATTACK AND FREE VALENCE IN COMPARISON WITH EXPERIMENTS

Compounds (Experimental position of attack)	Position	$f_r^{(R)}$	$S_r^{(R)}$	Free valence	$L_r^{(R)}$
Azulene	1	*0.299*	*1.186*	0.480	1.721
(1)	2	0.100	0.962	0.420	1.728
	4	0.246	1.132	*0.482*	*1.520*
	5	0.123	0.986	0.429	1.655
	6	0.261	1.105	0.454	1.620
	9	0.161	0.901	0.149	2.710
Fulvene	1	0.485	1.378	0.505	2.002
	2	0.216	1.091	0.434	2.238
	5	0.036	0.746	0.075	2.994
	6	*0.562*	*1.688*	*0.623*	*1.612*
Pentalene	1	*0.264*	*0.364*[a]	*0.558*	*1.959*
	2	0.263	0.363	0.432	2.027
	7	0.208	0.322	0.153	2.828
Heptalene	1	*0.183*	*0.303*[a]	*0.524*	*1.926*
	2	0.166	0.288	0.441	2.032
	3	0.167	0.289	0.494	2.026
	11	0.137	0.262	0.158	2.817
Fulvalene	1	*0.242*	*1.593*[b]	*0.510*	*1.676*
	2	0.180	1.402	0.498	1.848
	9	0.156	1.823	0.243	—
Acenaphthylene	1	*0.368*	*1.564*	0.37	*2.124*
(1 and 2)	3	0.195	1.046	0.41	2.262
	4	0.017	0.873	0.38	2.513
	5	0.238	1.112	*0.48*	2.193
	10	0.088	0.853	0.02	—
	11	0.088	0.947	0.11	—
	12	0.011	0.717	0.14	—
Fluoranthene	1	0.124	0.904	0.454	1.61
	2	0.069	0.798	0.398	1.82
	3	*0.284*	*1.139*	*0.470*	*1.54*
	7	0.136	1.066	0.438	1.71
	8	0.086	0.929	0.409	1.76

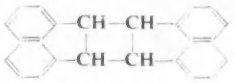
a) Calculated according to the modified formula of Eq. 27 of Ref. 7.
b) Calculated according to the formula of Eq. IV—4 of Ref. 7 (the constant term, $|\lambda_r|$ was omitted).

15) R. D. Brown, *J. Chem. Soc.*, **1959**, 2232.
16) A. G. Anderson, Jr., R. Scotoni, Jr., E. J. Cowles and C. G. Fritz, *J. Org. Chem.*, **22**, 1193 (1957); W. Treibs, *Angew. Chem.*, **67**, 70 (1955).
17) N. Campbell, W. W. Easton and J. Rayment, *Nature*, **165**, 76 (1950).
18) R. Tobler, T. Holbro, P. Sutter and W. Kern, *Helv. Chim. Acta*, **24**, 100 (1941).

electron theory agreed well with this fact because the values of frontier electron density and superdelocalizability at 3 and 8 positions are larger than the other positions. On the other hand, the total π-electron density method (the static method) predict 8 and 2 positions as the most susceptible to an electophilic attack, and localization method 3 and 7 positions. Other compounds such as fulvene, pentalene, heptalene and fulvalene have never been synthesized and accordingly no available experimental data have hitherto been obtained. The prediction of all indexes agreed entirely with each other in these compounds.

Reaction for a Radical Reagent.—In Table II, localization energy, frontier electron density and superdelocalizability for radical attack and the values of free valence were shown in comparison with known experimental data. For azulene the experiments showed that radical reagents attack position 1[19]. As is clearly seen in Table II, the values of frontier electron density and superdelocalizability explain the experimental fact well, whereas other indexes such as free valence and localization energy predict that position 4 will be the most reactive. Some doubts have been pointed out in connection with the reliability of the free valence as a chemical reactivity index[3,20]. Not a few cases appeared in which this index failed to explain the experiments; for example, in phenanthrene and 2-pentene[21]. On the other hand, localization energy has proved to be a good index in the case of alternant hydrocarbons. It may be of theoretical interest to observe in non-alternant hydrocarbons the inability of localization energy to explain the experimental results of, for example, the electrophilic reaction of fluoranthene and radical attack of azulene stated above.

Acenaphthylene has been found to make a colorless dimer, and it has been suggested that the mechanism of formation is not a simple "collisional" one, but depends on the existence of van der Waals complexes and Crawford and Coulson considered that the formation of these complexes is probably facilitated by the presence of a high free valence at the reacting carbon atoms. They calculated the free valence in this molecule and found that the values of 5, 6 positions are larger than that of 1, 2 positions[20]. On the other hand, experiments showed that the dimer has the following structure indicating that the 1, 2 positions have greater reactivity than 5, 6 positions[20,22].



Hence, the free valence, as is stated by Crawford and Coulson[20], is not a sufficient guide to reactivity. Frontier electron method and localization method both predict that the 1, 2 positions will be more reactive than 5, 6 positions. This result coincides with the experiment although there may remain some questions as to the applicability of the reactivity indexes to such a dimer-forming reaction.

TABLE III. FRONTIER ELECTRON DENSITY ($f_r^{(N)}$), SUPERDELOCALIZABILITY ($S_r^{(N)}$) AND LOCALIZATION ENERGY ($L_r^{(N)}$) FOR NUCLEOPHILIC ATTACK AND π-ELECTRON DENSITY (Q_r)

Compounds	Position	$f_r^{(N)}$	$S_r^{(N)}$	$L_r^{(N)}$	Q_r
Azulene	1	0.008	0.613	2.090	1.173
	2	0.199	0.907	1.728	1.047
	4	0.442	*1.559*	*1.231*	*0.855*
	5	0.021	0.937	1.655	0.986
	6	*0.522*	1.530	1.280	0.870
	9	0.169	0.851	—	1.027
Fulvene	1	0.246	0.906	2.002	1.092
	2	0.156	0.783	2.238	1.073
	5	0.073	0.597	2.994	1.047
	6	*1.124*	*2.701*	*0.984*	*0.623*
Pentalene	1	*0.500*	*1.000*[b]	*1.531*	*0.815*
	2	0.000	0.000	2.027	1.173
	7	0.000	0.000	—	1.198
Heptalene	1	0.032	0.529	2.193	1.125
	2	*0.332*	*1.401*	*2.032*	*0.882*
	3	0.000	0.401	2.357	1.119
	11	0.271	1.252	—	0.867
Fulvalene	1	0.123	1.835[b]	*1.365*	1.097
	2	*0.221*	*1.837*	1.452	*0.976*
	9	0.312	1.797	—	0.853
Acenaphthylene	1	0.208	0.861	2.124	1.066
	3	0.301	1.170	1.999	*0.909*
	4	0.029	0.719	2.513	1.008
	5	*0.356*	*1.191*	*1.969*	0.926
	10	0.106	0.664	—	1.044
	11	0.000	0.539	—	1.095
	12	0.000	0.616	—	0.998
Fluoranthene	1	0.243	1.028	1.46	*0.947*
	2	0.045	0.776	1.82	1.005
	3	*0.326*	*1.197*	*1.41*	0.958
	7	0.031	1.054	1.71	0.997
	8	0.079	0.793	1.76	1.008

a) See the first footnote of Table I.
b) Calculated according to the formula of Eq. IV—2 of Ref. 7 (the constant term, $2\lambda_{m+1}$, was omitted).

19) K. Hafner, *Angew. Chem.*, **70**, 419 (1958); H. Arnold and K. Pahls, *Chem. Ber.*, **89**, 121 (1956).
20) V. A. Crawford and C. A. Coulson, *J. Chem. Soc.*, **1948**, 1990.
21) S. Sato and R. J. Cvetanovic, *J. Am. Chem. Soc.*, **81**, 3223 (1959).
22) E. L. Bowen and L. D. F. Marsh, *J. Chem. Soc.*, **1947**, 109.

For other compounds such as fulvene, pentalene, heptalene, fulvalene and fluoranthene there are no available data. The prediction of the most reactive position of these molecules by theoretical indexes agreed entirely with each other.

Reaction for a Nucleophilic Reagent.—Braun and Manz heated fluoranthene and CuCN for 6 hr. at 260°C and got 3-CN derivative[23]. The nature of this reaction has not been determined. The reaction may be nucleophilic or otherwise radical in nature. Provided that the reaction proceeds in radical mechanism the theories agree with the experiment because free valence, localization energy, frontier electron density and superdelocalizability all predict position 3 as the most reactive, as is seen in Table II. On the other hand if the reagent attacks the substrate molecule as a nucleophilic reagent, the π-electron density method fails to predict the correct position as is shown in Table III, whereas the localization and frontier electron methods both succeed also in this case.

For other molecules no experiment seems to have been carried out and all indexes predict the same position as the most reactive center except for acenaphthylene and fulvalene. Some experimental information may be looked for in relation to acenaphthylene; position 5 is predicted by the localization method and the frontier electron method, and position 3 by π-electron density method. In the case of fulvalene, disagreement of predictions by the localization method and the static method has been pointed out by Brown[12] in connection with the "chemical non-crossing rule"; that is, the former predict position 1, whereas the latter, position 2. The frontier electron density and the superdelocalizability predict position 2 as the most reactive center toward nucleophilic reagents in agreement with the static method.

As was stated above, the static method fails to explain the experimental results of fluoranthene with regard to the electrophilic attack and the radical reaction of azulene and acenaphthylene. The localization method also could not correctly predict the position of attack in the case of electrophilic reaction of fluoranthene and radical reaction of azulene. On the other hand, the predictions by the frontier electron method were entirely consistent with experiments for all molecules so far tested.

Since no ambiguous parameter has been used in the calculations stated above, such a comparison of availability of various theoretical indexes may be of significance in the sense that it may be able to afford us a clue to search for the "true" feature of substitution process in conjugated molecules.

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23) J. V. Braun and G. Manz, *Ann.*, **488**, 111 (1931).

*The Formation and the Reactions of 3α-Chloro-5,6β-epoxy-5β-cholestane**

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(Received July 26, 1960)

The present paper describes a study on the configuration of the epoxide derived from 3α-chlorocholest-5-ene[1] by oxidation with monoperphthalic acid and also on the reaction of the epoxide with boron trifluoride-ether complex.

Oxidation of 3α-chlorocholest-5-ene with monoperphthalic acid gave an epoxide. The epoxide could not be reduced with lithium aluminum hydride in the usual way, but it was catalytically reduced with platinum oxide to afford, besides other products, 5β-cholestane (II) and 5β-cholestan-6β-ol (IIIa). The formation of the 5β-cholestane derivatives is of interest, and this reduction is analogous to the catalytic reduction of 5,6β-epoxy-5β-cholestan-3α-ol[2]. The reductive cleavage of the

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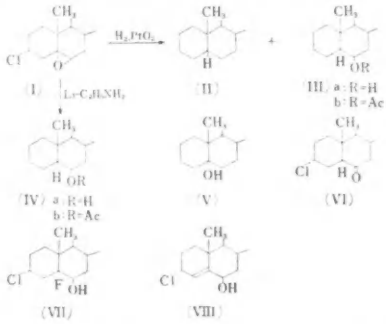
1) C. W. Shoppee and G. H. R. Summers, *J. Chem. Soc.*, **1952**, 1790.

2) Y. Urushibara and K. Mori, This Bulletin, **31**, 1068 (1958).

3α-chlorocholest-5-ene oxide with lithium-ethylamine[3] was also effected to give 5α-cholestan-6-β-ol (IVa) as the major product, along with an unsaturated material. In both of the above reductions, no 5α-cholestan-5-ol (V) was found in the products. On the basis of these observations, it was concluded that the epoxide is 3α-chloro-5,6β-epoxy-5β-cholestane



(I). An isomeric α-oxide was not obtained by the peracid oxidation of 3α-chlorocholest-5-ene.

The reaction of the epoxide with boron trifluoride-ether complex was investigated to complement the study by Henbest[4,5]. This lacks the reaction of a 3α-substituted 5,6β-epoxide with the reagent.

On treatment with boron trifluoride-ether complex, the epoxide was easily isomerized to 3α-chloro-5α-cholestan-6-one (VI) in a 35% yield. A "non-polar" oil[6] (13%) and an unsaturated substance (36%) were also produced. The yield of the 6-ketone was considerably lower than in the case of 3α-acetoxy-5,6α-epoxy-5α-cholestane[7]. It is probably because the resulting 6-ketone is a 5α-cholestane derivative (cis migration of C_6-hydrogen[4]) with 3α-chlorine and the 3-axial substituent decreases the yield of the 6-ketone. Since 5β-cholestane-3,6-dione was not transformed into 5α-cholestane-3,6-dione under the same condition, 3α-chloro-5α-cholestan-6-one was formed directly from 3α-chloro-5,6β-epoxy-5β-cholestane and, therefore, the above assignment of a β-configuration to the epoxide is further confirmed.

The formation of a diaxial fluorohydrin (5α-fluoro,6β-hydroxy) (VII) was probably discouraged because 1,3-diaxial interaction between 3α-chlorine and 5α-fluorine was involved.

3) A. S. Hallsworth, H. B. Henbest and T. I. Wrigley, *J. Chem. Soc.*, **1957**, 1969, 4604.
4) H. B. Henbest and T. I. Wrigley, ibid., **1957**, 4596.
5) H. B. Henbest and T. I. Wrigley, ibid., **1957**, 4765.
6) An oily substance which was not adsorbed on alumina.

Experimental****

3α-Chloro-5,6β-epoxy-5β-cholestane (I).—A mixture of 200 mg. of 3α-chlorocholest-5-ene and 2 equivalents of monoperphthalic acid in 10 ml. of dry ether was allowed to stand at room temperature overnight. The solution was washed with 5% aqueous sodium hydroxide and then with water to neutral reaction. Removal of the solvent from the dried (sodium sulfate) solution afforded a colorless crystalline residue. Recrystallization from methanol gave 120 mg. of 3α-chloro-5,6β-epoxy-5β-cholestane in needles, m. p. 98~99°C. Filtration through alumina, followed by recrystallization from methanol, raised the m. p. to 101.5~103°C. $[\alpha]_D^{15}$ −7° (*c* 2.65, chloroform).

Found: C, 77.06; H, 10.92. Calcd. for $C_{27}H_{45}ClO$: C, 77.01; H, 10.77%.

Reductive Cleavage of the Epoxide I.—*Catalytic Reduction.*—A mixture of 150 mg. of I and 20 mg. of Adams platinum oxide in 10 ml. of acetic acid was agitated with hydrogen at room temperature. In 1.5 hr. the hydrogen uptake was complete (2 mol.). The catalyst was removed by filteration and the solvent was evaporated under reduced pressure. The colorless oily residue was acetylated in the usual way and the product was chromatographed on 4.5 g. of alumina. Fractions eluted with petroleum ether gave oily residues (108 mg. in total), some of which were crystallized from methanol to give 3 mg. of 5β-cholestane (II), m. p. 63~65°C (recrystallized from methanol) and 20 mg. of 5β-cholestan-6β-ol acetate[7] (IIIb), m. p. 108~108.5°C (recrystallized three times from methanol; the yield of the crude product was 46 mg.). These compounds were identified by the mixed melting point test with authentic samples. Further elution of the column with benzene-petroleum ether (1:9) afforded a small amount of a halogen-containing substance in needles, m. p. 117~124°C, which was not further investigated. The oily residues from other fractions failed to crystallize, and 5α-cholestan-5-ol was not isolated from them.

Reduction with Lithium-Ethylamine.—A solution of 150 mg. of I in 4.3 g. of ethylamine was treated with 100 mg. of lithium at room temperature. A deep blue color appeared after 20 min., and persisted during 40 min. The reaction product was isolated according to the procedure of Benkeser[8] to give 137 mg. of a pale yellow oily product, which gave a yellow color with tetranitromethane and showed a negative Beilstein test. The oil (81 mg.) was acetylated in the usual way and the resulting yellow oil (80.5 mg.) was treated with monoperphthalic acid, and the resulting epoxide was subjected to hydrolytic cleavage with phosphomolybdic acid[9]. An oily product (75.4 mg.), which did not give a yellow color with tetranitromethane, was chromatographed on 2.1 g. of alumina, and from the fractions

**** All melting points were not corrected.
7) D. N. Jones, J. R. Lewis, C. W. Shoppee and G. H. Summers, ibid., **1955**, 2876.
8) R. A. Benkeser, R. E. Robinson, D. M. Sauve and O. H. Thomas, *J. Am. Chem. Soc.*, **77**, 3230 (1955).
9) By this procedure, the unsaturated material was converted into a 1,2-*trans*-glycol (M. Sawai, presented at the 10th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1957).

eluted with petroleum ether, 43.9 mg. of an oily residue was obtained. This was crystallized from methanol to give 34 mg. of 5α-cholestan-6β-ol acetate[10] (IVb) in needles, m. p. and mixed m. p. 74~75°C. The amount of the unsaturated material in the above reduction products was estimated by catalytic reduction. From the amount of hydrogen uptake, it was inferred that the unsaturated material amounted to about 30% of the total.

Attempted Reduction with Lithium Aluminum Hydride.—I was treated with lithium aluminum hydride at the boiling point of ether in the usual way, but the reduction was not effected. An attempt to effect the reduction at the boiling point of benzene was also unsuccessful.

Reaction of I with Boron Trifluoride-Ether Complex.—Freshly distilled boron trifluoride-ether complex (4 drops) was added to a solution of 200 mg. of I in 20 ml. of dry benzene. After 4 min. at room temperature, the solution was treated with aqueous sodium bicarbonate, and washed with water. Removal of the solvent from the dried (sodium sulfate) solution afforded a semi-solid residue, which was crystallized from acetone to give 3α-chloro-5α-cholestan-6-one (VI), m. p. 178~180°C. Under the same condition, 5β-cholestane-3,6-dione was not converted into 5α-cholestane-3,6-dione.

The chromatography of the above semi-solid residue (200 mg.) afforded 26.9 mg. of a "non-polar" oil, 69 mg. of 3α-chlorocholestan-6-one, and 73.2 mg. of an oily material. The oily substance gave an intense yellow color with tetranitromethane and showed a positive Beilstein test and hydroxyl infrared absorption. Since it was readily acetylated in the usual way, and the 3α-chlorine in 3α-chlorocholest-5-ene and in 3α-chloro-5α-cholestan-6-one was not eliminated with boron trifluoride-ether complex to give unsaturated compounds, it is probable that the oily material consisted mainly of 3α-chlorocholest-4-en-6β-ol (VIII).

The authors express their thanks to Professor Y. Urushibara of the University of Tokyo for his valuable advice, and to Mrs. Y. Fujita for her assistance in the preliminary course of this study. The authors are also indebted to the Ministry of Education for the Grant in Aid for the Fundamental Scientific Research.

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10) C. W. Shoppee and G. H. R. Summers, *J. Chem. Soc.*, **1952**, 3361.

Studies on Pyridotropolones. VI[1]*. Rearrangement Reactions of Brominated 8-Isopropyl-pyrido[3, 2-d]tropolones to 7-Isopropyl-6-quinolinols*

By Kameji YAMANE

(Received July 13, 1960)

Previously the author[2] reported that nitroso-, amino-, quinoxalo- and oxazolo-compounds were obtained from 2-methyl-8-isopropyl-pyrido[3, 2-*d*]tropolone. The present work was carried out for the purpose of elucidating the chemical reactivity of pyrido[3, 2-*d*]tropolone, and the rearrangement reactions of brominated 8-isopropyl-pyrido[3, 2-*d*]tropolones to 7-isopropyl-6-quinolinols were studied.

Bromination of 2-methyl-8-isopropyl-pyrido-[3, 2-*d*]tropolone (Ia) with 1 molar equivalent of NBS gave 5-bromo-compound IIa. IIa showed brownish yellow coloration in benzene layer with ferric chloride solution. Heating IIa in 2 N potassium hydroxide solution afforded pale yellow (nearly colorless) needles, m. p. 229.5~230°C (IIIa), 2-methyl-8-isopropyl-pyrido-[3, 2-*d*]-tropolone (Ia) and a red oily matter. IIIa gave no Beilstein test, whose analytical values agreed with formula $C_{13}H_{15}ON$. Its ultraviolet absorption spectrum (Fig. 1) closely resembled that of 6-quinolinol[3]. The infrared spectrum of IIIa exhibited several absorption bands (2980 cm^{-1} for CH stretching vibrations, 1530, 1568, 1607 and 1630 cm^{-1} for C=C and C=N streching vibrations, and 1245 cm^{-1} for phenolic OH deformations). Furthermore, the compound IIIa readily underwent some typical electrophilic substitution reactions. Namely, IIIa was readily brominated in acetic acid solution to form a monobromo compound

1) This work was presented at the 13th Annual Meeting of the Chemical Society of Japan, Tokyo, April 1960.
2) K. Yamane, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **80**, 1175 (1959).
3) G. W. Ewing and E. A. Steck, *J. Am. Chem. Soc.*, **68**, 2181 (1946).

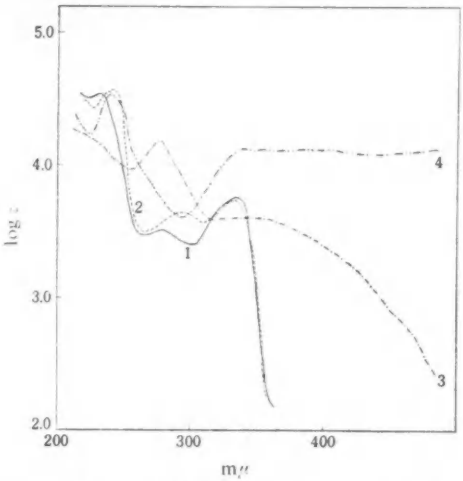


Fig. 1. Ultraviolet absorption spectra (in methanol).

1: 2-Methyl-7-isopropyl-6-quinolinol (IIIa)
2: 2-Methyl-5-bromo-7-isopropyl-6-quinolinol (IVa)
3: 2-Methyl-5-nitroso-7-isopropyl-6-quinolinol (Va)
4: 2-Methyl-5-(*p*-tolylazo)-7-isopropyl-6-quinolinol (VIa)

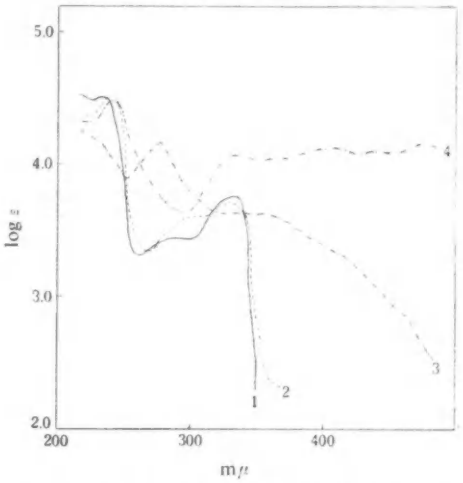


Fig. 3. Ultraviolet absorption spectra (in methanol).

1: 7-Isopropyl-6-quinolinol (IIIb)
2: 5-Bromo-7-isopropyl-6-quinolinol (IVb)
3: 5-Nitroso-7-isopropyl-6-quinolinol (Vb)
4: 5-(*p*-Tolylazo)-7-isopropyl-6-quinolinol (VIb)

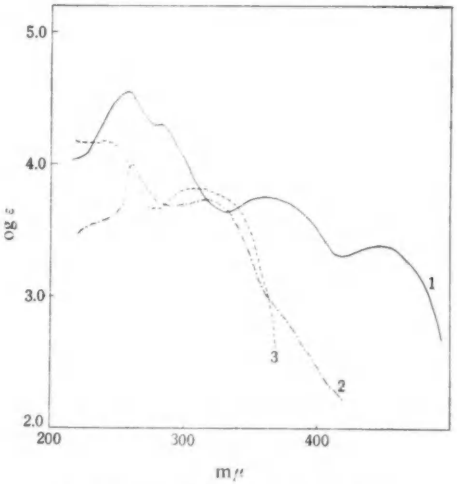


Fig. 2. Ultraviolet absorption spectra.

1: 2-Methyl-5-bromo-8-isopropyl-pyrido-[3,2-*d*]tropolone (IIa) (in methanol)
2: Dibromo-compound VIIa (in carbon tetrachloride)
3: Dibromo-compound VIIa (in methanol)

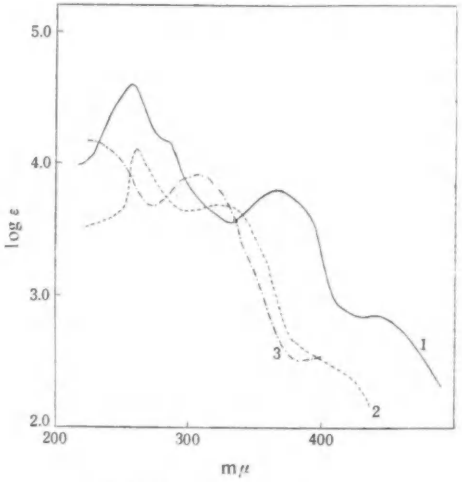
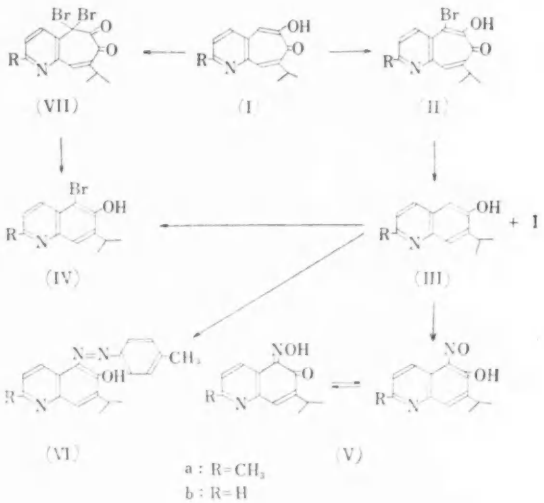


Fig. 4. Ultraviolet absorption spectra.

1: 5-Bromo-7-isopropyl-pyrido[3,2-*d*]-tropolone (IIb) (in methanol)
2: Dibromo-compound VIIb (in carbon tetrachloride).
3: Dibromo-compound VIIb (in methanol)

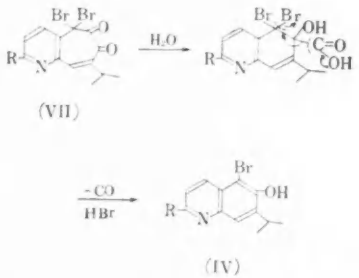
(IVa). Nitrosation of IIIa in acetic acid solution gave nitroso compound Va. The compound IIIa coupled with diazotized *p*-toluidine in alkaline solution to yield an azo compound VIa. From these facts shown above, IIIa was assumed to be 2-methyl-7-isopropyl-6-quinolinol.

Bromination of 2-methyl-8-isopropyl-pyrido-[3, 2-*d*]tropolone gave dibromo compound as yellow rhombic prisms, m. p. 129~130°C (VIIa). The analytical values of this compound agreed with formula $C_{11}H_{12}O_2NBr_3$, and its ultraviolet absorption spectrum (Fig. 2) differed from that of 2-methyl-5-bromo-8-isopropyl-pyrido[3, 2-*d*]tropolone (IIa). Moreover, the infrared spectrum of VIIa exhibited two bands at 1742 and 1684 cm^{-1} due to the carbonyl group, and no bands in the hydroxyl region. The compound VIIa was unstable against water, acid, alkali and alcohols. In fact when heated with water, it dissolved gradually under foaming and gave 2-methyl-5-bromo-7-isopropyl-6-quinolinol (IVa) which was obtained by bromination of IIIa described above. Heating VIIa with 1 N hydrochloric acid also gave IVa in good yield. VIIa, however, gave 2-methyl-5-bromo-8-isopropyl-pyrido[3, 2-*d*]tropolone (IIa) when it was heated with 2 N potassium hydroxide solution. These facts indicated that the dibromo compound VIIa possessed the structure shown as *o*-diketone formula (VIIa).



8-Isopropyl-pyrido[3, 2-*d*]tropolone (Ib)[4] showed almost the similar reactions as in the case of Ia. Namely, Ib was readily brominated with NBS to form 5-bromo-compound (IIb) and dibromo compound (VIIb). Heating IIb in 2 N potassium hydroxide solution afforded 7-isopropyl-6-quinolinol (IIIb). IIIb afforded bromo compound (IVb), nitroso compound (Vb) and *p*-tolylazo-compound (VIb). Furthermore VIIb was rearranged to 5-bromo-7-isopropyl-6-quinolinol (IVb) when treated with water or 1 N hydrochloric acid, and or 2 N potassium hydroxide solution.

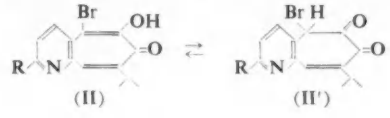
It is thought that the mechanism of this interesting rearrangement of VII to 5-bromo-7-isopropyl-6-quinolinols (IV) goes on first through benzilic acid rearrangement, followed by decarboxylation and dehydrobromination as follows:



In the case of the rearrangement reaction of 5-bromo-8-isopropyl-pyrido[3, 2-*d*]tropolones (II) to 7-isopropyl-6-quinolinols (III) with potassium hydroxide solution, it is thought

4) K. Yamane, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **81**, 509 (1960).

that II undergoes rearrangement in like manner as VII via its tautomeric structure II'.



(II) (II')

Experimental

2-Methyl-5-bromo-8-isopropyl-pyrido[3,2-*d*]tropolone (IIa).—A mixture of 0.2 g. of 2-methyl-8-isopropyl-pyrido[3,2-*d*]-tropolone (Ia) and 0.18 g. of NBS in 4 cc. of carbon tetrachloride was refluxed for 2 hr. After cooling, succinimide and the solvent were removed and the residue was recrystallized from ethanol to give 0.25 g. of yellow needles, m. p. 145~145.5°C.

Found: C, 54.37; H, 4.65; N, 4.84. Calcd. for $C_{14}H_{14}O_2NBr$: C, 54.54; H, 4.58; N, 4.55%.

5-Bromo-8-isopropyl-pyrido[3,2-*d*]tropolone (IIb).—A mixture of 0.7 g. of 8-isopropyl-pyrido-[3,2-*d*]tropolone (Ib) and 0.64 g. of NBS in 40 cc. of carbon tetrachloride was refluxed for 2 hr. After cooling, succinimide and the solvent were removed and the residue was recrystallized from ethanol to give 0.72 g. of yellow needles, m. p. 155.5~156°C.

Found: C, 53.22; H, 4.02; N, 4.92. Calcd. for $C_{13}H_{12}O_2NBr$: C, 53.07; H, 4.11; N, 4.76%.

2-Methyl-7-isopropyl-6-quinolinol (IIIa).—a) A solution of 1 g. of IIa in 3 cc. of 2 N potassium hydroxide solution was heated for 2 hr. on a water bath. After cooling, 10 cc. of water was added and acidified with 1 N hydrochloric acid to deposite dark brown precipitates. The precipitates were collected and sublimated, yielding yellow sublimates, which were recrystallized from ethanol in pale yellow needles, m. p. 127~128°C, about 0.1 g. These did not depress by admixture with 2 methyl-8-isopropyl-pyrido[3,2-*d*]tropolone (Ia). The mother liquor of the dark brown precipitates was evaporated on a water bath to dryness and the residue was extracted with acetone. Acetone extracts were purified by passing through an alumina column to give about 30 mg. of crystals. Recrystallization from alcohol gave pale yellow (nearly colorless) needles, m. p. 229.5~230°C.

Found: C, 77.32; H, 7.19; N, 6.84. Calcd. for $C_{13}H_{15}ON$: C, 77.58; H, 7.51; N, 6.96%.

b) A solution of 0.4 g. of IIa in 3 cc. of 2 N potassium hydroxide solution was heated on a water bath for 2 hr. After cooling, the solution was slightly acidified with acetic acid to deposit brown precipitates (20 mg., m. p. 240°C). The filtrate of the precipitates was evaporated on a water bath to dryness and the residue was sublimated to give 130 mg. of pink prisms. Recrystallization from alcohol gave red needles, m. p. 228~229°C, undepressed by admixture with IIIa. Furthermore, the red needles were dissolved in acetone and purified by passing through an alumina column to give pale yellow (nearly colorless) needles, m. p. 229~230°C.

7-Isopropyl-6-quinolinol (IIIb).—A solution of 0.4 g. of IIb in 2.3 cc. of 2 N potassium hydroxide solution was heated on a water bath and acidified with 2 N hydrochloric acid to deposite pale brown precipitates. The precipitates were recrystallized from methanol to give yellow needles, m. p. 160~161°C, undepressed by admixture with Ib. Mother liquor of the pale brown precipitates was evaporated on a water bath to dryness and the residue was extracted with acetone. Acetone extracts were purified by passing through an alumina column to give colorless plates, m. p. 193°C. Yield 90 mg.

Found: C, 76.67; H, 6.85; N, 7.46. Calcd. for $C_{12}H_{13}ON$: C, 76.97; H, 7.00; N, 7.48%.

Picrate, yellow plates, m. p. 229~230°C (decomp.) from methanol.

Found: N, 13.43. Calcd. for $C_{18}H_{16}O_8N_4$: N, 13.46%.

2-Methyl-5-bromo-7-isopropyl-6-quinolinol (IVa).—To a solution of 0.13 g. of IIIa in 2 cc. of acetic acid, a solution of 0.1 g. of bromine in 0.5 cc. of the same solvent was added dropwise with stirring. When the addition had been nearly completed some yellow crystals were deposited. After removal of the crystals, water was added and neutralized with ammonia to give precipitates, which were recrystallized from dilute alcohol in pale yellow (nearly colorless) needles, m. p. 129~130°C.

Found: C, 55.84; H, 4.79; N, 4.92. Calcd. for $C_{13}H_{14}ONBr$: C, 55.72 H, 5.04; N, 5.00%.

5-Bromo-7-isopropyl-6-quinolinol (IVb).—To a solution of 20 mg. of IIIb in 0.5 cc. of acetic acid, 20 mg. of bromine dissolved in 0.5 cc. of the same solvent was added dropwise with stirring. After standing for 2 hr., water was added and neutralized with ammonia to give colorless precipitates, which were recrystallized from acetone in pale yellow needles, m. p. 128~129°C. Yield about 25 mg.

Found: C, 54.04; H, 4.26; N, 5.24. Calcd. for $C_{12}H_{12}ONBr$: C, 54.15; H, 4.55; N, 5.26%.

2-Methyl-5-nitroso-7-isopropyl-6-quinolinol (Va).—To a solution of 0.15 g. of IIIa in 1 cc. of acetic acid, a solution of 0.08 g. of sodium nitrite in a small amount of water was added dropwise. The yellow crystals that separated out were collected by filtration and washed with water. Yield 0.15 g. Recrystallization from methanol yielded yellow prisms, m. p. 181°C (decomp.).

Found: C, 67.76; H, 5.72; N, 11.59. Calcd. for $C_{13}H_{14}O_2N_2$: C, 67.81; H, 6.13; N, 12.17%.

5-Nitroso-7-isopropyl-6-quinolinol (Vb).—To a solution of 41 mg. of IIIb in 1 cc. of acetic acid, 23 mg. of sodium nitrite in a small amount of water was added dropwise. The yellow crystals that separated out were collected by filtration and washed with water. Recrystallization from methanol yielded bright yellow scales, m. p. 156°C (decomp.). Yield about 45 mg.

Found: C, 66.66; H, 5.76; N, 13.02. Calcd. for $C_{12}H_{12}O_2N_2$: C, 66.65; H, 5.59; N, 12.96%.

2-Methyl-5-(*p*-tolylazo)-7-isopropyl-6-quinolinol (VIa).—To a cold solution of 45 mg. of *p*-toluidine in 2 cc. of 3 N hydrochloric acid, a solution of 42 mg. of sodium nitrite in 0.5 cc. of water was dropped, and the resultant cold diazonium solution was added dropwise to the cold solution of 80 mg. of IIIa in 10 cc. of 2 N-potassium hydroxide solution. The red precipitates thereby formed were collected by filtration. These were recrystallized from methanol

in orange red needles, m. p. 109.5~110°C. Yield 90 mg.

Found: C, 75.46; H, 6.35; N, 13.57. Calcd. for $C_{16}H_{15}ON_3$: C, 75.21; H, 6.63; N, 13.16%.

5-(*p*-Tolyl-azo)-7-isopropyl-6-quinolinol (VIb).—A cold solution of diazonium salt prepared from 35 mg. of *p*-toluidine, 1 cc. of 3 N hydrochloric acid and 55 mg. of sodium nitrite was added dropwise to a solution of 60 mg. of IIIb in 2 cc. of 2 N sodium hydroxide solution. The reddish brown precipitates which formed were recrystallized from methanol in red needles, m. p. 122~123°C. Yield 50 mg.

Found: C, 74.62; H, 6.02; N, 13.92. Calcd. for $C_{19}H_{19}ON_3$: C, 74.73; H, 6.27; N, 13.76%.

Bromination of 2-Methyl-8-isopropyl-pyrido[3, 2-*d*]tropolone (Ia) with 2 Molar Equivalents of NBS. (Dibromo-Compound VIIa).—A mixture of 1.43 g. of Ia and 2.21 g. of NBS in 30 cc. of carbon tetrachloride was refluxed on a water bath for 2 hr. After cooling, succinimide and the solvent were removed, the residue was recrystallized from carbon tetrachloride to give 1.16 g. of yellow rhombic prisms, m. p. 129~130°C.

Found: C, 43.37; H, 3.56; N, 3.56. Calcd. for $C_{14}H_{11}O_2NBr_2$: C, 43.44; H, 3.39; N, 3.62%.

Bromination of 8-Isopropyl-pyrido[3, 2-*d*]tropolone (Ib) with 2 Molar Equivalents of NBS. (Dibromo-Compound VIIb).—A mixture of 1.72 g. of Ib and 2.85 g. of NBS in 100 cc. of carbon tetrachloride was refluxed on a water bath for 2 hr. After cooling, succinimide and the solvent were removed, and the residue was recrystallized from chloroform or carbon tetrachloride to give 2.21 g. of dibromo compound VIIb in yellow polyhedrones, m. p. 142~143°C.

Found: C, 42.09; H, 2.90; N, 3.69. Calcd. for $C_{13}H_{11}O_2NBr_2$: C, 41.85; H, 2.97; N, 3.76%.

Rearrangement Reaction of Dibromo Compound VIIa to 2-Methyl-5-bromo-7-isopropyl-6-quinolinol (IVa).—**a) By Water.**—When a mixture of 0.39 g. of dibromo compound VIIa and 3 cc. of water was heated on a water bath, VIIa slowly dissolved under foaming. The mixture was further heated for 2 hr. After removal of a small amount of brownish yellow resinous matter which appeared during the heating, the solution gradually deposited orange needles (hydrochloride of IVa) on standing. The needles were dissolved in 6 cc. of hot water and neutralized with 2 N potassium hydroxide solution to give precipitates, which were recrystallized from dilute alcohol in pale yellow (nearly colorless) needles, m. p. 129~130°C. Yield, 0.1 g. No depression in m. p. was observed on admixture of 2-methyl-5-bromo-7-isopropyl-6-quinolinol (IVa) which was obtained by bromination of IIIa described above.

b) By 1 N Hydrochloric Acid.—A mixture of 0.39 g. of VIIa and 3 cc. of 1 N hydrochloric acid solution was heated on a water bath for 30 min. On cooling, 0.31 g. of yellow crystals, m. p. 223~224°C (decomp.) were obtained. The crystals were dissolved in 5 cc. of hot water and neutralized with a 2 N potassium hydroxide solution to give colorless precipitates, which were recrystallized from dilute methanol in pale yellow (nearly colorless) needles, m. p. 129~130°C. Yield, 0.13 g. The needles were undepressed on admixture with IVa.

Reaction of Dibromo Compound VIIa with 2 N Potassium Hydroxide Solution.—When 0.16 g. of VIIa was mixed with 0.68 cc. of 2 N potassium hydroxide solution, an exothermic reaction began immediately to give a dark greenish yellow solution. After being heated for 20 min., the solution was slightly acidified with acetic acid to give yellow precipitates, which were recrystallized from alcohol in yellow prisms, m. p. 145~146°C, undepressed by admixture with 2-methyl-5-bromo-8-isopropyl-pyrido-[3,2-*d*]tropolone (IIa). Yield, about 0.04 g.

Rearrangement Reaction of Dibromo Compound VIIb to 5-Bromo-7-isopropyl-6-quinolinol (IVb).—**a) By Water.**—A mixture of 0.37 g. of VIIb and 1 cc. of water was heated on a water bath for 2 hr. After cooling, a small amount of water was added and neutralized with 2 N potassium hydroxide solution to deposit brown precipitates. Recrystallization from acetone yielded 0.17 g. of colorless needles, m. p. 128.5~129°C. No depression in m. p. was observed on admixture with the authentic sample of IVb which was obtained by bromination of IIIb described above.

b) By 1 N Hydrochloric Acid.—A mixture of 0.37 g. of VIIb and 3 cc. of 1 N hydrochloric acid solution was heated on a water bath for 1 hr. After cooling, the resultant red solution was neutralized with a 2N potassium hydroxide solution to give precipitates, which were recrystallized from acetone in colorless needles, m. p. 127~128°C. Yield 0.2 g. The needles also were undepressed on admixture with the authentic sample of IVb.

c) By 1 N Potassium Hydroxide Solution.—A mixture of 0.3 g. of VIIb and 3 cc. of 1 N potassium hydroxide solution was heated on a water bath for 10 min. After cooling, the mixture was neutralized with acetic acid to give brown precipitates, which were recrystallized from acetone in pale yellow needles, m. p. 129°C. The mother liquor was evaporated on a water bath to dryness and the residue was extracted repeatedly with acetone. The extracts were purified by passing through an alumina column. After removal of the solvent, the residue was crystallized from a dilute acetone to yield another crop of yellow needles, m. p. 129°C. Total yield 43 mg. These were found to be identical with IVb by mixed fusion.

The author takes this opportunity to express his sincere gratitude to Professor T. Nozoe (Tohoku University) and Professor A. Yokoo for their guidance and encouragement. Thanks are also due to Assistant Professor J. Iwasa for measurements of infrared spectra. The author is also grateful to Mrs. K. Kodaira, Mr. S. Azumi and Miss A. Iwanaga (Nozoe laboratory) for measurements of ultraviolet spectra and for carrying out micro analyses, and to Mr. Y. Shimoyama for his cooperation in these experiments.

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Partition Equilibria of 2-Methyl 5-Ethyl Pyridine in the Systems of Benzene-Water and Chloroform-Water

By Tokio KATO and Yasugoro TSUNODA

(Received February 27, 1960)

It is well known that 2-methyl 5-ethyl pyridine (M. E. P.) is prepared through the condensation of paraldehyde with aqueous ammonia[1], where benzene and chloroform are used to extract M. E. P. from the reaction product[2,3].

This paper presents a brief discussion on the partition equilibria of M. E. P. in the above-mentioned systems.

Experimental

A thermostat adjusted to ±0.1°C, and conical flasks of 300 cc. with tight stoppers were used. M. E. P. was prepared by catalytic condensation of paraldehyde with aqueous ammonia[1]. The crude M. E. P. was rectified for several times; b. p. 74°C/20 mmHg, n_D^{20}, 1.4966.

Benzene and chloroform were rectified, and their boiling points were 80~81°C and 61~62°C respectively. Several solutions, being varied in concentration of M. E. P. (less than 3.0 mol./l.) in benzene and chloroform (50 cc.) were prepared in the flasks. Distilled water (150 cc.) was added to each of them, and they were settled for a certain time after being subjected to vigorous shaking every 5~6 min.

Each group of five samples was brought side by side in the thermostat for 2 hr. at 10, 20, 30, 40 and 50°C, and used for analysis.

The concentration of M. E. P. was easily determined by titration with N/2 HCl, where methyl orange was used as an indicator.

Volumes of samples employed for analysis were 5 cc. for benzene and chloroform layer and 100 cc. for the aqueous layer, where the former was titrated in the mixed solvent (100 cc.) of isopropyl benzene and ethylene glycol.

Results and Discussion

In Fig. 1 (2), C_1 and C_2 are the concentrations of M. E. P. in benzene (chloroform) and aqueous layers and both of them were calculated from volumes of consumed N/2 HCl (cc.), while titrating volumes were corrected by blank tests.

In the system of benzene-water, the constancy of $K(C_2/C_1)$ with the change of C_1 or C_2 at each temperature is confirmed, and the linear relation between $\log K$ and $1/T$ (T: absolute temperature, °K) shown in Fig. 3 suggests that it satisfies the following thermodynamic formula.

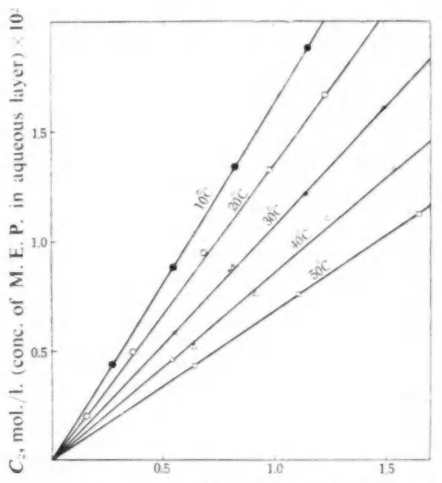

Fig. 1. Equilibrium concentrations of M. E. P. in benzene and water.

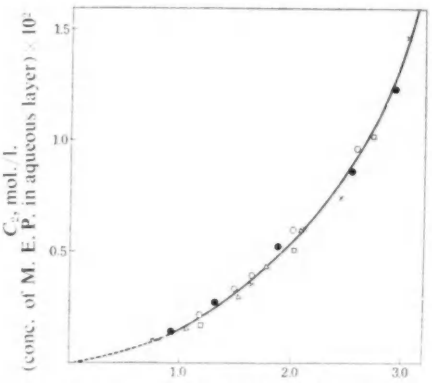

Fig. 2. Equilibrium concentrations of M. E. P. in chloroform and water.

● 10°C ◎ 20 〃 × 30 〃 △ 40°C □ 50 〃

1) U. S. Pat., 2,615,022 (1952).
2) U. S. Pat., 2,703,804 (1955).
3) U. S. Pat., 2,769,007 (1956).

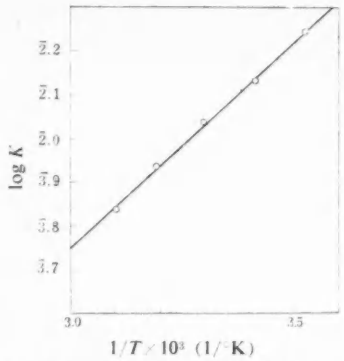

Fig. 3. Equilibrium constant K (benzene-water).

$$\ln K_2/K_1 = -Q/R(1/T_1 - 1/T_2)$$

where R is gas constant, and Q the heat of transference of 1 mol. M. E. P. from benzene to water under equilibrium state.

Thus Q was determined to be 4.3 kcal./mol. Therefore the equilibrium constant K of M. E. P. between benzene and water satisfies the following formula

$$K = 7.7_0 \times 10^{-6} e^{2.19 \times 10^3/T}$$

In the system of chloroform-water, the parabolic relation between C_1 and C_2 was found (Fig. 2) and the constancy of K ($\sqrt{C_2}/C_1$) at each temperature was confirmed, as shown in Fig. 4.

This means that the molecular weight of M. E. P. in chloroform is half of that in water

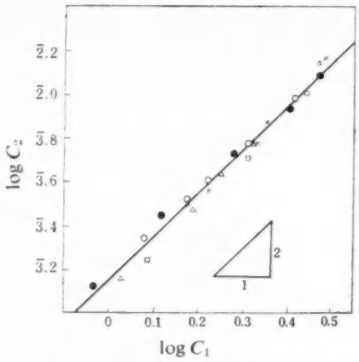

Fig. 4. Linear relation of $\sqrt{C_2}$ to C_1 (chloroform-water).

●— 10°C —△— 40°C
—○— 20 〃 —□— 50 〃
—×— 30 〃

or benzene, so the molecules of M. E. P. in latter solvents seem to associate with each other. Furthermore, the values of K in each temperature are uniformly equal to 3.7×10^{-2}, and their changes with temperatures (10~50°C) are negligibly small.

The authors are grateful to Dr. H. Sobue, Professor of the Tokyo University and Dr. A. Tomita, chief of the Laboratory Institute, for their valuable advice.

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On the Reaction of Aromatic Dinitriles and Formaldehyde

By Toshihisa TACHIKAWA

(Received June 20, 1960)

The nitrile group is known to be hydrolysed to acid amide according to the following mechanism,

$$R\text{-}C{\equiv}N \xrightarrow{HCl} R\text{-}\underset{\underset{Cl}{|}}{C}{=}NH$$

$$R\text{-}\underset{\underset{Cl}{|}}{C}{=}NH \xrightarrow{H_2O} R\text{-}\underset{\underset{OH}{|}}{C}{=}NH + HCl$$

$$R\text{-}\underset{\underset{OH}{|}}{C}{=}NH \longrightarrow R\text{-}CONH_2$$

the reaction being caused by the polar structure of nitrile group. Therefore it is possible to synthesize the compounds having amide linkage by the reaction between nitrile compounds and the compounds which form carbonium cation readily. If the compounds having two nitrile radicals in a molecule are used as the starting material, it is possible to synthesize macromolecules having amide linkages.

Magat[1] and Ritter[2] have studied such

1) E. E. Magat, *J. Am. Chem. Soc.*, **73**, 1028, 1367 (1951).
2) J. J. Ritter, ibid., **70**, 4045 (1948).

reactions. Magat synthesized the polyamide known as 1,6-nylon having the following structure by reacting adiponitrile and formaldehyde in concentrated sulfuric acid at normal temperature

$$n\,CN(CH_2)_4CN + n\,CH_2O \rightarrow CN\text{-}(CH_2)_4\text{-}CONHCH_2NHCO(CH_2)_4\cdot CONHCH_2NHCO(CH_2)_4\text{-}]_n CN$$

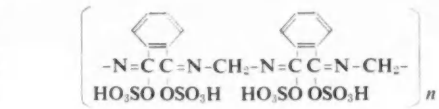
It is reported that this compound had the following properties: m. p. 225°C, mol. wt., 10,000~20,000 (by the osmotic pressure method) and the intrinsic viscosity $[\eta_{sp}/c] = 0.7 \sim 1.3$ (solvent: *m*-cresol). Magat also reported that this compound had good solvent resistance and fiber-forming ability. In his study on the dinitriles, aliphatic dinitriles have been used, but aromatic dinitriles have not been studied. However, it is probable that a new characteristic polyamide having a benzene nucleus and -CONH- linkage will be obtained by the reaction of the aromatic dinitrile and the formaldehyde.

In the present paper the reaction of aromatic dinitriles such as ortho-, iso-, tere-phthalonitrile and *p*-xylylene cyanide, with the formaldehyde has been investigated by means of Magat's method and as a result the author has been able to syntnesize a new polyamide having benzene nucleus and -CONH- linkages.

The condensation polymers having -CONH- linkages in the molecule are obtained from all the above dinitriles except orthophthalonitrile. Condensation polymer from terephthalonitrile and formaldehyde has the largest intrinsic viscosity.

Results and Discussion

In the reaction of aromatic dinitriles and formaldehyde in concentrated sulfuric acid, the effect of the substituted position of two nitrile groups is shown in Table I. In the case of orthophthalonitrile, it does not react with formaldehyde. This is believed to be due to the steric hindrance of the neighboring two nitrile groups in the intermediate polymer in the sulfuric acid.



In the case of terephthalonitrile on the other hand, it reacts easily with formaldehyde without the effect of steric hindrance and the product which has the highest condensation polymerization degree is formed. Further, *p*-xylylene cyanide with difficulty causes condensation polymerization reaction with formaldehyde. This is believed to be due to the high reactivity of the methylene hydrogen between the nitrile groups and the benzene nucleus of *p*-xylylene cyanide, which easily causes the side reaction with formaldehyde.

The infrared absorption spectra of the isophthalonitrile and the terephthalonitrile condensation polymer is shown in Fig. 1.

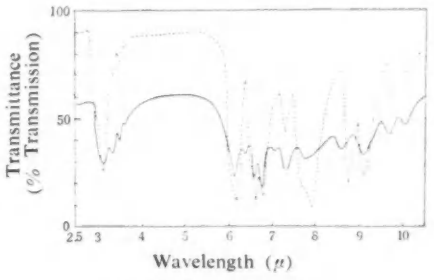


Fig. 1. Infrared spectra

—— Isophthalonitrile + $(HCHO)_n$ polymer

---- Terephthalonitrile + $(HCHO)_n$ polymer

As shown in Fig. 1, a C≡N stretching vibration at 4.5 μ disappears and an N-H stretching vibration at 3.05, 3.30, 3.45 μ, an N-H deformation vibration at 6.6 μ and a C=O stretching vibration at 6.1 μ appears as in 6,6-nylon. Furthermore, a $-CH_2-$ deformation vibration at 6.75 μ is observed. So it is now clear that both of these polymers have -CONH $-CH_2-NHCO-$ linkages, as expected. The result of elementary analysis indicated that these polymers have the following structures;

Table I. Reaction conditions and results

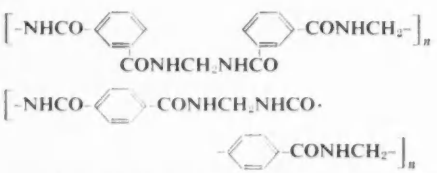
Nitriles (g.)	HCHO (g.)	95% H_2SO_4 (g.)	React. temp. (°C)	React. periods (hr.)	Product (g.)	η_{sp}/c
Ortho- 11.30	2.75	90.70	20	3	No product	—
Iso- 11.30	2.75	90.70	20	3	Condensation polymer 15.0	0.258
Tere- 11.30	2.75	90.70	20	3	Condensation polymer 15.0	0.443
p-Xylylene 4.70	1.00	30.00	20	3	Condensation polymer 6.1	—

TABLE. II. SOLUBILITY

Solvents	Isophthalonitrile polymer		Terephthalonitrile polymer		*p*-Xylylene cyanide polymer	
	Under room temp.	Under heating	Under room temp.	Under heating	Under room temp.	Under heating
95% Sulfuric acid	Sol.	Sol.	Sol.	Sol.	Sol.	Sol.
85% Phosphoric acid	Sol.	Sol.	Insol.	Insol.	Insol.	Insol.
90% Formic acid	Insol.	Insol.	〃	〃	〃	〃
Acetic acid	〃	〃	〃	〃	〃	〃
Monochloroacetic acid	〃	〃	〃	〃	〃	〃
Methyl alcohol	〃	〃	〃	〃	〃	〃
Acetone	〃	〃	〃	〃	〃	〃
Ethyl ether	〃	〃	〃	〃	〃	〃
Chloroform	〃	〃	〃	〃	〃	〃
Chlorobenzene	〃	〃	〃	〃	〃	〃
Benzene	〃	〃	〃	〃	〃	〃
n-Hexane	〃	〃	〃	〃	〃	〃
Phenol	〃	Sol.	〃	〃	〃	〃
m-Cresol	〃	Sol.	〃	〃	〃	〃
Carbon disulfide	〃	Insol.	〃	〃	〃	〃
Dimethyl formamide	Sol.	Sol.	〃	〃	〃	〃
Dimethyl sulfoxide	Sol.	Sol.	〃	〃	〃	〃
Aniline	Insol.	Insol.	〃	〃	〃	〃
Pyridine	〃	〃	〃	〃	〃	〃

TABLE III. EFFECT OF ADDITION CONDITION

Addition condition	η_{sp}/c
Adding terephthalonitrile into the sulfuric acid solution of formaldehyde.	0.229
Adding paraformaldehyde into the the sulfuric acid solution of terephthalonitrile.	0.174
Adding the mixture of terephthalonitrile and paraformaldehyde into the sulfuric acid.	0.428



From these findings, it is understood that the aromatic dinitrile compounds are also capable of forming polyamide as in the case of aliphatic dinitrile compounds.

As benzene rings and –NHCO– linkages are arranged alternately in such polyamide, the crystallization will be accelerated by the intermolecular hydrogen bonds between –CONH– groups and the molecules will be oriented easily. The insolubility of these condensation polymers in almost all organic solvents as shown in Table II and the higher decomposition point above 300°C without melting or softening may be attributed to this crystalline structure.

In concentrated sulfuric acid, aromatic dinitrile is easily hydrolysed into acid amide and formaldehyde forms carbonium cation and becomes very reactive. Therefore, it is believed that the molar ratio between these two reagents

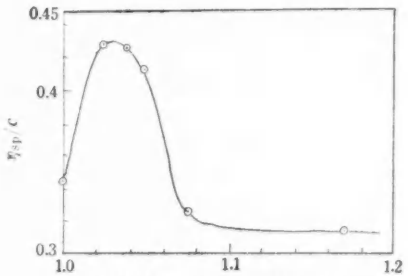
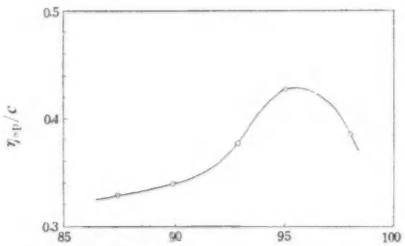


Fig. 2. Effect of the molar ratio of formaldehyde to terephthalonitrile.

greatly influences the condensation polymerization reaction in sulfuric acid. As shown in Fig. 2 and Table III, the product which has the highest condensation polymerization degree is obtained when the equimolecular mixture of terephthalonitrile and formaldehyde is added into sulfuric acid.

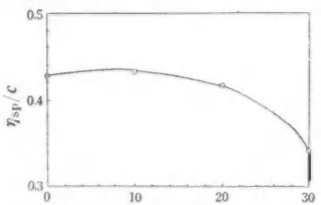
When terephthalonitrile is added into the sulfuric acid solution of formaldehyde and when the molar ratio of formaldehyde to terephthalonitrile is large, formaldehyde is always in excess to the dinitrile in the reaction

solution. In this condition the side reaction with activated formaldehyde becomes so predominant that the condensation polymerization reaction is impeded and consequently the intrinsic viscosity of the reaction product becomes low. Similarly when formaldehyde is added into the sulfuric acid solution of terephthalonitrile and the molar ratio is small, the intrinsic viscosity of the reaction product becomes low. It is considered that this fact is due to the hydrolysis of terephthalonitrile into terephthalamide. It is probably for the same reason that the condensation polymerization product of great intrinsic viscosity can not be obtained when the concentration of sulfuric acid is lower than 95% and the reaction temperature is higher, as shown in Figs. 3 and 4.



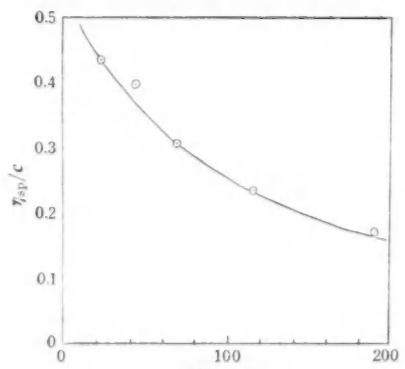
Concentration of sulfuric acid, %

Fig. 3. Effect of concentration of sulfuric acid.



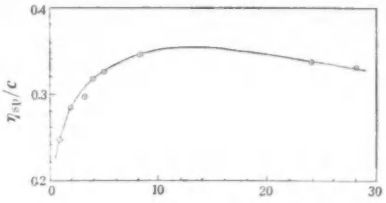
Reaction temperature, °C

Fig. 4. Effect of reaction temperature.



Time, hr.

Fig. 5. Degradation by sulfuric acid.



Time, hr.

Fig. 6. Effect of reaction time.

The condensation polymer from terephthalonitrile and formaldehyde rapidly degrades in the presence of sulfuric acid at room temperature as shown in Fig. 5. This behavior is somewhat unexpected since the condensation polymer itself is prepared in the concentrated sulfuric acid. Although the mechanism of degradation is not clear, -CONH- linkage may be hydrolysed by acid. As it is probable that the condensation polymerization reaction is accompanied by a simultaneous degradation reaction, the degree of condensation polymerization of the product becomes lower when the reaction time is longer, as shown in Fig. 6.

On the other hand no condensation polymer can be obtained by reacting terephthalamide with formaldehyde under the same reaction conditions as in the case of the terephthalonitrile. Thus it is clear that the mechanism of this reaction is not considered as the formation of acid amide by the hydrolysis of nitrile group in sulfuric acid followed by the methylol condensation as in urea resins, but is considered as follows.

$$CH_2O + H_2SO_4 \rightarrow CH_2OH^+ + HSO_4^-$$

$$CN\text{-}C_6H_4\text{-}CN + CH_2OH^+ + HSO_4^- \rightarrow CN\text{-}C_6H_4\text{-}C(OSO_3H)=N\cdot CH_2OH \quad (I)$$

$$I + H_2SO_4 \rightarrow CN\text{-}C_6H_4\text{-}C(OSO_3H)=N\cdot CH_2^+ \quad (II) + HSO_4^- + H_2O$$

$$II + HSO_4^- + CN\text{-}C_6H_4\text{-}CN \rightarrow CN\text{-}C_6H_4\text{-}C(OSO_3H)=N\cdot CH_2\cdot N=C(OSO_3H)\text{-}C_6H_4\text{-}CN$$

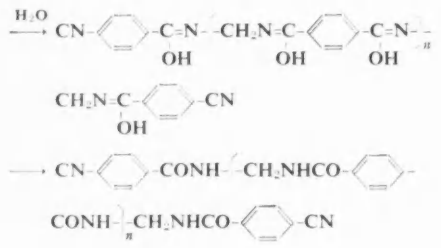
$$\vdots$$

$$CN\text{-}C_6H_4\text{-}C(OSO_3H)=N\text{-}CH_2N=C(OSO_3H)\text{-}C_6H_4\text{-}C(OSO_3H)=N\text{-}$$

$$CH_2N=C(OSO_3H)\text{-}C_6H_4\text{-}CN$$

TABLE IV. ELEMENTARY ANALYSIS

Dinitrile	Found			Calcd.			
	C	H	N	C	H	N	
Isophthalonitrile	58.6	4.7	15.5	61.4	4.6	15.9	for $(C_9H_5N_2O_2)_n$
Terephthalonitrile	58.9	4.7	16.6	61.4	4.6	15.9	for $(C_9H_5N_2O_2)_n$
p-Xylylene cyanide	62.3	6.0	13.0	64.7	5.9	13.7	for $(C_{11}H_{12}N_2O_2)_n$



Experimental

Synthesis of Orthophthalonitrile. — Phthalamide was prepared from phthalic anhydride and aqueous ammonia by the standard method, and then phthalamide (68 g.) was dehydrated to phthalonitrile with acetic anhydride (425 g.) in chlorobenzene (88 g.) by the known method[3]. Yield 26.5 g. (50% of theoretical yield). After recrystallizing from water, a colorless crystal was obtained, m. p. 141~142°C.

Sntheysis of Isophthalonitrile. — Isophthalyl chloride was prepared from isophthalic acid and thionyl chloride, and transformed to isophthalamide with aqueous ammonia. Isophthalamide (32.8 g.) and phosphorus pentachloride (41.6 g.) were mixed in chlorobenzene (200 g.) and the mixture was heated gradually. It was heated for an hour at 98°C. until a homogeneous solution was obtained. After pouring the solution into ice water, 20 g. of crude isophthalonitrile was obtained with 78% yield. The crude material was recrystallized from water. The pure material melted at 160.5°C.

Synthesis of Terephthalonitrile.—Terephthalyl chloride was prepared from terephthalic acid and phosphorus pentachloride and transformed to terephthalamide with aqueous ammonia and then terephthalamide was dehydrated to terephthalonitrile with phosphorus pentachloride in chlorobenzene, using the same methods as in the case of the isophthalonitrile. The crude terephthalonitrile was recrystallized from benzene to needle crystals, m. p. 221.5~222.0°C.

Synthesis of *p*-Xylylene Cyanide.—A solution of potassium cyanide (13 g.) in 25 g. of water was added dropwise into a solution of *p*-xylene bromide (13 g.) in 200 cc. of ethanol at 80°C and the mixture was heated under reflux for three hours. After the reaction was completed, ethanol was distilled off and the residue was poured into ice water and filtered. The precipitate was recrystallized from ethanol and hot water to get pure *p*-xylylene cyanide (4.7 g.), m. p. 96~97.5°C.

3) E. Koike; *J. Chem. Soc. Japan. Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **57**, 925 (1954).

Condensation Polymerization of Aromatic Dinitriles and Formaldehyde.—A mixture of paraformaldehyde and dinitriles was added in small portions with stirring at a constant temperature into sulfuric acid which was placed in a 100 cc. three-necked flask equipped with thermometer and stirrer. External cooling was necessary to maintain the constant temperature at 0°C because the reaction was exothermic. After the exothermic reaction was over, the mixture began to thicken gradually. The stirring was continued for two hours after the nitrile was added, to complete the reaction. The reaction product was poured into ice water with stirring to precipitate the condensation polymer. The precipitate was washed with water and the remaining acid was removed by washing with sodium bicarbonate solution (1%), then it was dried at 60°C until it was posssible to get constant weight under reduced pressure. The result of the elementary analysis is shown in Table IV.

Infrared Absorption Spectrum.—A specimen film of the condensation polymer of isophthalonitrile was prepared by evaporating the *m*-cresol solution of the polymer under reduced pressure. The specimen film of the condensation polymer of terephthalonitrile was prepared by squeezing the viscous reaction product between the two glass plates followed by washing the thin layer of polymer with water. The clear thin film thus obtained was dried under reduced pressure. The infrared absorption spectra were observed on these films using a Perkin-Elmer Model 21 spectrophotometer.

Intrinsic Viscosity.—Four hundred milligrams of the condensation polymer was added into 1000 cc. of 85% sulfuric acid and dissolved completely. This was left at 11~12°C for 24 hr. with shaking. The specific viscosity was measured on this solution by using Ostwald's viscosimeter at 30°C and the intrinsic viscosity was calculated.

The Reaction of Terephthalamide and Formaldehyde.—A mixture of terephthalamide (8.2 g.) and paraformaldehyde (1.5 g.) was added into concentrated sulfuric acid (98%, 75 g.) with stirring at 20°C. Although the stirring was continued for two hours after addition, the viscosity of the reaction mixture did not increase. When the reaction mixture was poured into the ice water, white precipitates (8.0 g.) were obtained.

Found: C, 58.41; H, 4.99; N, 17.10. Calcd. for $C_9H_5N_2O_2$: C, 58.53; H, 4.91; N, 17.07%

Summary

1. Like aliphatic dinitriles, polyamide having benzene nucleus and –CONH– linkages was synthesized by condensation polymerization reaction of aromatic dinitriles and formaldehyde in concentrated sulfuric acid.

2. The condensation polymer obtained from terephthalonitrile had the greatest intrinsic viscosity among ortho-, iso-, tere-phthalonitrile and *p*-xylylene cyanide. A product of the highest condensation polymerization degree was obtained, by adding the 1.025 : 1 molar mixture of paraformaldehyde and terephthalonitrile in small portions into ten molar amounts of 95% sulfuric acid at 0°C and then stirring for ten hours at the same temperature.

3. These condensation polymers were insoluble in almost all organic solvents and had no melting and softening point. They decomposed above 300°C.

The author wishes to express his sincere thanks to Professor Ryozo Goto of Kyoto University for his kind advice, and also to Mr. Murataro Nakashima, President of Kunoshima Chemical Co., for his permission to publish this paper.

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*Ultraviolet Spectra of N-Heterocyclic Systems. I. The Anions of Uracils**

By Koji NAKANISHI, Noboru SUZUKI and Futaba YAMAZAKI

(Received July 26, 1960)

The keto-enol equilibria of uracil and its anions have been studied in order to clarify the nature of the tautomerism encountered in the complicated derivatives of a natural product[1,2]. Moreover, besides being of interest because of its relation to nucleic acids, uracil contains two potentially dissociable protons, and accordingly it was felt that this simple molecule might provide a convenient means for more complex systems. The keto-enol equilibria of various monohydroxy *N*-heterocyclic bases have already been studied extensively by means of infrared, ultraviolet, and Raman spectroscopy, and other methods[3]. The studies with dihydroxy compounds are much more limited, and although the phenomena have indeed been investigated with uracil, especially by Shugar and Fox[4], the tautomeric equilibrium constants K_T were not taken into consideration.

Six tautomeric forms are conceivable for uracil. However, the following evidence shows that it exists predominantly in the diketo form I (Plate 1) in solution as well as in the solid state. The solid infrared spectrum of uracil (Table I) in the double bond stretching region is very similar to 1, 3-dimethyluracil (VIII) which has a fixed structure; 1-methyluracil (IV) and 3-methyluracil (VI), for which three tautomeric forms are possible, respectively, also show very similar absorptions. The dioxane solution spectra of uracil, 1-methyluracil, and 3-methyluracil are also quite similar to 1, 3-dimethyluracil. Hence, it is easily seen that all four compounds can be represented by the diketo forms both in dioxane and in the solid state. It is well-known that among the possible tautomers, the more polar forms are favored in the solid state and in solutions of high dielectric constants. The fact that the tautomers present in dioxane, a solvent of low dielectric constant (2.101 at 25°C)[5], and in the solid state, are the diketo forms (I, IV, VI) suggests that the same diketo forms are also predominant

TABLE I. INFRARED ABSORPTIONS (in cm^{-1})

	KBr	Dioxane
Uracil (I)	1715, 1670	1720 sh, 1698
1-Methyluracil (IV)	1695, 1675	1712 sh, 1694
3-Methyluracil (VI)	1705, 1630	1726, 1670
1, 3-Dimethyluracil (VIII)	1712, 1655	1713, 1673

* Paper read in part at the 13th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1960.

1) K. Nakanishi, M. Ohashi, S. Kumasaki and S. Yamamura, *J. Am. Chem. Soc.*, **81**, 6339 (1959).

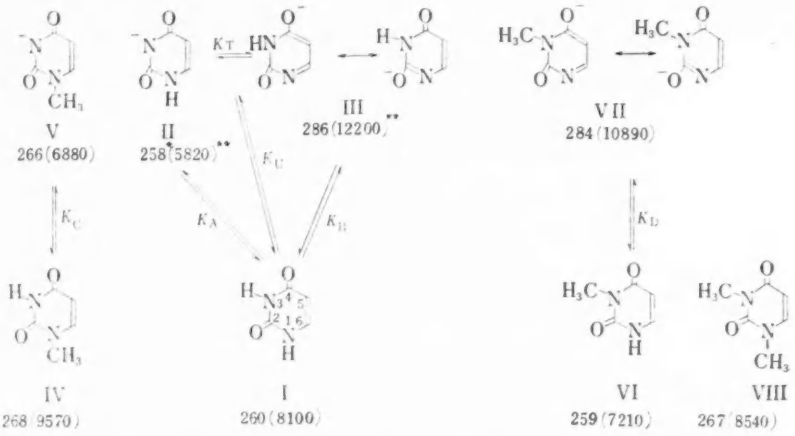
2) Results pertaining to the natural derivatives will be reported shortly.

3) Some recent papers on this subject: (a) H. Shindo, *Chem. and Pharm. Bull.*, **7**, 407 (1959); (b) K. Nakamoto and A. E. Martell, *J. Am. Chem. Soc.*, **81**, 5857 (1959); (c) A. Albert and E. Spinner, *J. Chem. Soc.*, **1960**, 1221.

4) D. Shugar and J. J. Fox, *Biochem. et Biophys. Acta*, **9**, 199 (1952); see also J. J. Fox and I. Wempen in "Advances in Carbohydrate Chemistry", Vol. 14, Academic Press, New York (1959), p. 283.

5) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions", Reinhold Publishing Co., New York (1958), p. 161.

Plate 1. Proton equilibria of uracils in water



Data for neutral molecules and anions are for pH 6.86 and 12.0, respectively.
Peak positions (mμ) and intensities (ε) are given.
* Obtained after wing correction (Fig. 4).
** Calculated (see text).

TABLE II. ULTRAVIOLET SPECTRA OF URACILS (25°C)
Wavelengths given in mμ; numbers in parentheses are $\varepsilon \times 10^{-3}$
$\Delta\lambda$ (in mμ) = λ (pH 12.0) − λ (pH 6.86)

		Dioxane	pH 6.86	pH 9.71	pH 12.0	$\Delta\lambda$	pK
1.	Uracil	257(8.35)	260 (8.10)	265(5.47)	286 (6.01)	+26	9.51 (at 25°C)
2.	Thymine[a)]		265 (7.89)		291 (5.44)	+26	9.9
3.	1-Methyluracil	266(9.70)	268 (9.57)	267(7.64)	266 (6.88)	− 2	9.77 (at 25°C)
4.	Uridine[a)]		262(10.1)		262 (8.5)	0	9.25
5.	Uracil deoxyriboside[a)]		262(10.2)		262 (7.63)	0	9.3
6.	Thymidine[a)]		267 (9.65)		267 (7.38)	0	9.8
7.	3-Methyluracil	257(7.31)	259 (7.21)	255(5.74)	284(10.89)	+25	10.00 (at 25°C)
8.	1,3-Dimethyl uracil	265(8.71)	267 (8.54)				

a) Data from D. Shugar and J. J. Fox, *Biochem. et Biophys. Acta*, **9**, 199 (1952).

in water, a solvent of higher dielectric constant[6]. This was supported by measuring the ultraviolet spectra in dioxane-water mixtures. Isosbestic points, suggestive of an equilibrium mixture, were absent, and in all cases the only trend observed was a slight red shift in going from 100 percent dioxane to water (pH 6.86, Table II, intermediate dioxane concentrations are omitted); it is well-known that in neutral uncharged molecules the $\pi-\pi^*$ bands are shifted towards the red as the dielectric constant of the solvent is increased.

The ultraviolet spectra are recorded in Figs. 1—3. In going from the neutral to the anionoid

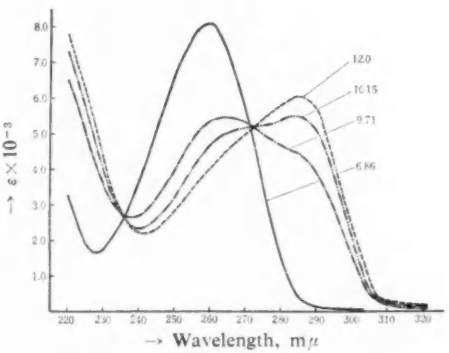


Fig. 1. Ultraviolet spectra of uracil at various pH (numbers beside curves).

6) Infrared measurements have shown that uridine and uridylic acid exist in the diketo form in D_2O: H. T. Miles, *Biochim. et Biophys. Acta*, **22**, 247 (1956).

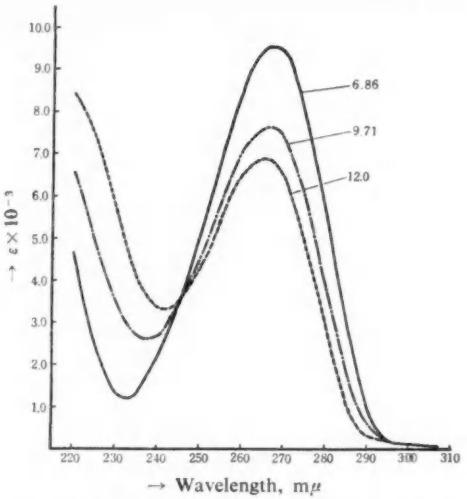


Fig. 2. Ultraviolet spectra of 1-methyluracil at various pH (numbers beside curves).

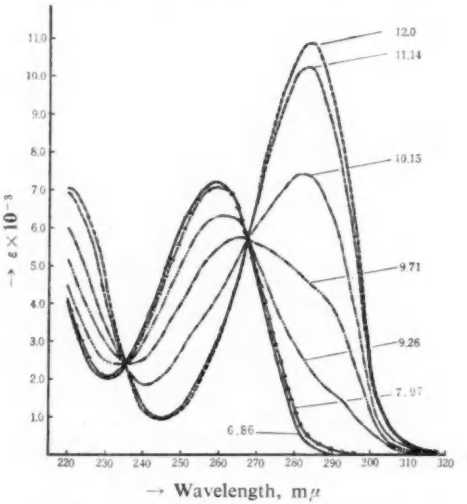
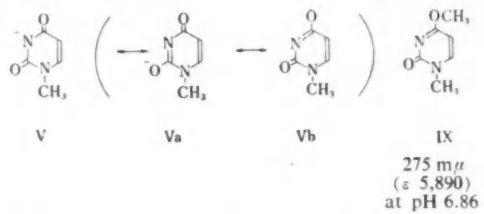
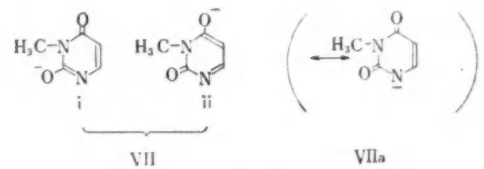


Fig. 3. Ultraviolet spectra of 3-methyluracil at various pH (numbers beside curves).

species in the case of 1-methyluracil, the peak intensity is lowered, but the wavelength is almost unaffected (Fig. 2 and Table II). This rules out the contribution of canonical structures such as Va or Vb; because of a more extended conjugated system, Va and Vb should show absorption at much longer wavelengths than the original species. For example, 1-methyl-4-methoxy-2-pyrimidone (IX) (cf., Experimental), which contains the O=C–N=C–OCH_3 system, already absorbs at 275 mμ, and accordingly Va and Vb containing the O=C–N=C–O^- system would be expected to show absorption at a still longer wavelength. Localization of the negative charge on the nitrogen atom has recently been suggested for the anion of 2-hydroxypyridine[8]. The cause for this localization is probably due to the fact that the intrinsic stability of the two carbonyl bonds outweigh the stabilization gained by an extended conjugation. Similar trends, i.e., lowering of peak intensity and constancy or slight blue shift of band position, are encountered upon anion formation in other 1-substituted uracils (Table II, nos. 4—6) and various uridine phosphates[9] such as uridine-5′-diphosphate (262 mμ, ε 10,000 vs. 261 mμ, 7,900), and uridine-5′-triphosphate (262 mμ, ε 10,000 vs. 261 mμ, 8,100). The anion of 3-methyluracil, on the other hand, shows a considerable red shift and increases in peak intensity. This behavior can be accounted for by canonical structures VII-i or VII-ii[10] but not by VIIa; in VII a conjugated system more extended than Va or Vb is present, and this probably compensates for the carbonyl bond energy.





The anion of uracil (Fig. 1) has its peak at 286 mμ (ε 6,010) with a broad hump around 260 mμ (ε ca. 4,000). The peak undoubtedly corresponds to the 284 mμ (ε 10,890) peak of VII; if wing correction (Fig. 4) is carried out by subtracting the curve of 3-methyluracil anion multiplied by 6,010/10,890, a peak is revealed at 258 mμ (ε 2,490). This peak is due to the anion II, the equivalent of V (266 mμ). Thus, the following empirical rule is apparent

7) H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952).
8) E. Spinner, *J. Chem. Soc.*, **1960**, 1232.
9) R. M. C. Dawson, D. C. Elliott, W. H. Elliott and K. M. Jones, ed., "Data for Biochemical Research," Oxford Univ. Press, London (1959), p. 78.
10) At present, no conclusion can be drawn as regards the relative weights of contributions of structures VII-i and VII-ii.

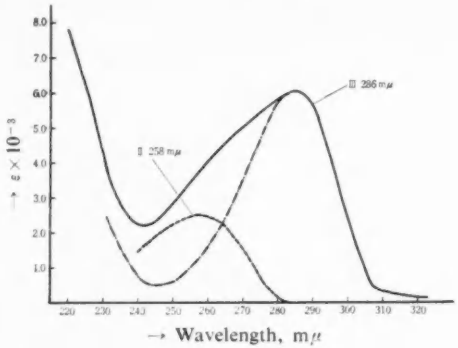


Fig. 4. Ultraviolet absorptions of uracil anions at pH 12.0.

in the ultraviolet spectra of uracils (Plate 1, see also Table II): (1) Alkylation at N-1 results in a red shift of ca. 8 mμ (I vs. IV, II vs. V). (2) Deprotonation at N-1 similarly results in a red shift of ca. 26 mμ (I vs. III, VI vs. VII). (3) Alkylation at N-3 results in a slight blue shift of 1~2 mμ (I vs. VI, III vs. VII). (4) Deprotonation at N-3 similarly results in a slight blue shift of ca. 2 mμ (IV vs. V, I vs. II). It is interesting to note that this simple calculation is also applicable to the disubstituted 1, 3-dimethyluracil (VIII): calculated λ_{max} 266~267 mμ; observed 267 mμ. The ultraviolet absorption curves of thymine (5-methyluracil) and thymidine[10] show that this general trend is apparent in this series also.

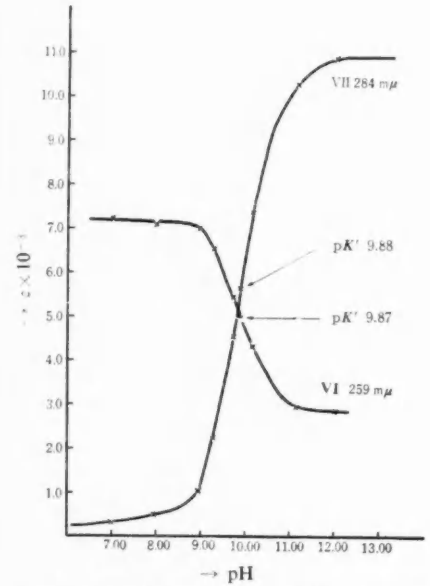


Fig. 5. 3-Methyluracil; variation of peak intensities with pH.

The pK of uracil (pK_U), 1-methyluracil (pK_C), and 3-methyluracil (pK_D) were obtained by spectroscopic measurement of the pK' from the curves at pH 6.86, 9.71 and 12.0 (Figs. 1—3), and correction to thermodynamic pK values (Table II). The pK' values were also obtained by graphical plotting of extinction coefficients versus pH as shown in Fig. 5 for 3-methyluracil; the results are identical with the calculated values and, therefore, are omitted for other samples. The extinction coefficients for the anions II and III, which cannot be obtained experimentally, were calculated as follows:

$$\varepsilon_{III}/\varepsilon_{I} = \varepsilon_{VII}/\varepsilon_{VI}$$

hence, $\varepsilon_{III} = 8100 \times 10890/7210 = 12200$

and the percentage of III present in the uracil anion is

$$\text{III (percentage)} = 6010/12200 \times 100 = 49$$

Accordingly, the ratio of II to III, K_T, is $51/49 = 1.0$.

Similarly,

$$\varepsilon_{II}/\varepsilon_{I} = \varepsilon_{V}/\varepsilon_{IV}$$

hence, $\varepsilon_{II} = 8100 \times 6880/9570 = 5820$

The percentage of II may be estimated from the intensity of the 258 mμ peak (Fig. 4):

$$\text{II (percentage)} = (2490/5820) \times 100 = 43$$

hence, $K_T = \text{II}/\text{III} = 43/57 = 0.8$

The agreement with the ratio 1.0 calculated from the 286 mμ peak is not quite satisfactory, but the 1.0 value is probably more correct because no wing correction is necessary.

If K_A and K_B are the individual dissociation constants leading from I to II and III, respectively (Plate 1), it can be readily shown[11] that

$$K_u = K_A + K_B \quad \text{and} \quad K_T = \text{II}/\text{III} = K_A/K_B$$

Substitution of $K_T = 1.0$ gives $pK_A = pK_B = 9.81$.

Occasionally[11,12], K_T is calculated by assuming that K_C or K_D is approximately equal to K_A or K_B, respectively, since substitution of a methyl group for a hydrogen atom would have a minor effect. However, the above results show that the approximation is not so satisfactory. Since the ultraviolet spectra of the other compounds listed in Table II and of the uridine phosphates[9] closely resemble those of the uracils treated in the present paper, the tautomeric behavior can be handled in an identical manner.

11) G. F. Tucker and J. L. Irvin, *J. Am. Chem. Soc.*, **73**, 1923 (1951).

12) E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides," Reinhold Publ. Corp., New York (1943), p. 96.

Experimental

Materials.—1-Methyluracil[13] was prepared from uracil through 2,4-dichloropyrimidine, 2,4-dimethoxypyrimidine and 1-methyl-4-methoxy-2-pyrimidone (hydrolysis). The structure of the product as 1-methyluracil has been confirmed by Brown et al.[14].

3-Methyluracil[15] was prepared from ethyl ethoxy methylenemalonate[16] through 3-methyl-5-carbethoxyuracil and 3-methyl-5-carboxyuracil(decarboxylation). Product confirmed by Brown et al.[14]

1,3-Dimethyluracil[17] was prepared by methylation of uracil with dimethyl sulfate.

Spectral Measurements.—The infrared spectra were recorded with a Koken model 301 spectrophotometer. The ultraviolet spectra were recorded with a Hitachi model EP-1 spectrophotometer; a pair of 1 cm. quartz cells with stoppers was used and the cell temperature was maintained at 25±1°C. The error in absorbancy is ±0.002.

Measurement of p*K*.—All pH measurements were carried out at 25±1°C with a Horiba model P pH meter equipped with extension glass and calomel electrodes; the meter was calibrated with a standard Horiba buffer solution of pH 6.86 at 25°C(KH_2PO_4+Na_2HPO_4). The following buffers were used for the pH indicated: pH 7.97, KH_2PO_4+Na_2HPO_4; pH 8.95, 9.26, 9.71 and 10.15, Na_2CO_3+$NaHCO_3$; pH 11.14 and 12.0 (uncorrected), Na_2HPO_4+NaOH. The ionic strength of the solutions was 0.1. The apparent pK' was calculated from:

$$pK' = pH - \log (\varepsilon_{HX} - \varepsilon_{obs})/(\varepsilon_{obs} - \varepsilon_X)$$

where ε_{HX} and ε_X are the molecular extinction coefficients (ε) measured in pH 6.86 and pH 12.0 buffer solutions, respectively, and ε_{obs} is the ε measured in an intermediate pH solution where the pH was chosen so that the value of $(\varepsilon_{HX} - \varepsilon_{obs})/(\varepsilon_{obs} - \varepsilon_X)$ was near unity, i. e., pH 9.71. The wavelength chosen was 260 mμ and 285 mμ for uracil, 265 mμ for 1-methyluracil, and 259 mμ and 284 mμ for 3-methyluracil.

The pK' was also obtained graphically as shown in Fig. 5. These apparent constants were corrected to the thermodynamic scale with the aid of the Debye-Hückel relationship,

$$pK = pK' + \log f_{HX} - \log f_X \quad (1)$$

$$\log f_X = -0.509(\sqrt{I}/1+\sqrt{I}) \text{ (at 25°C)}$$

where f and I represent the activity coefficient and the ionic strength. Since for neutral molecules f_{HX} is approximately unity, the correction becomes

$$pK = pK' - \log f_X = pK' + 0.12$$

Summary

In aqueous solutions uracil exists predominantly in the diketo form, whereas in alkaline solutions it exists as an approximately 1:1 mixture of two deprotonated forms. The two deprotonated anions show ultraviolet absorptions similar to the anions of 1-methyluracil and 3-methyluracil, and the main contributing canonical structures which give rise to the general absorption feature of the anions are discussed. The peak shifts accompanying N-alkylation or deprotonation may be summarized in a simple empirical rule. Individual ionization constants have also been estimated.

The results of uracil can be extended to thymine, uridine, thymidine, and their phosphates. The pesent method can probably be extended to other systems containing two dissociable protons.

The authors are indebted to Professor F. Egami, the University of Tokyo, for his initial suggestion of the problem and interests. Part of the expenses have been covered by the Grant in Aid for Fundamental Scientific Research, Ministry of Education.

Department of Chemistry
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13) G. E. Hilbert and T. B. Johnson, *J. Am. Chem. Soc.*, 52, 2001 (1930).
14) D. J. Brown, E. Hoerger, and S. F. Mason, *J. Chem. Soc.*, 1955, 211.
15) C. E. Whitehead, *J. Am. Chem. Soc.*, 74, 4267 (1952).
16) "Organic Syntheses", Coll. Vol. 3, John Wiley and Sons, Inc., New York (1955), p. 395.
17) D. Davidson and O. Baudisch, *J. Am. Chem. Soc.*, 48, 2382 (1926).

Secondary Electron Emission from Copper-Beryllium (4%) Surface by Bombardment of Various Positive Ions

By Toshio SUGIURA and Teruo HAYAKAWA

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According to the development of the mass spectrometric investigations, the necessities for the measurements of the minute ion intensity are rapidly increasing. The secondary electron multiplier has now widely been used as an excellent ion detector for the measurements of ionization potentials and the microanalysis of many isotopes. Many reports on the secondary electron emission from the metal surfaces by the bombardment of high energy ions were already published. But unfortunately, some results of them disagree with each other[1,2], and these discrepancies might be caused by the different surface conditions of the ion targets for the secondary electron emission.

Recently, Hagstrum[3-6] has reported the many important results of the Auger ejection process of secondary electrons from the atomically clean surfaces of transition metals by the bombardment of the noble gas ions, and he suggested that the existence of the adsorbed layer causes the remarkable influence on the mechanism of the secondary electron ejection. But the target surfaces are not always atomically clean under the ordinary operating conditions, and the influence of the adsorbed layer seems considerably complicated since the semiconductor surfaces are usually used for obtaining the large electron yield.

The characteristics necessary for the secondary electron multiplier are the large electron yield per impinged ion or electron and the excellent stability for the electron yield under the usual operating conditions. The electron yield mainly depends upon the following factors:

(1) the mass, energy, electronic charge and configuration of the incident particle;

(2) the chemical and physical properties of the metal surface; and

(3) the angle with which the incident particle strikes the metal surface.

The present investigation was undertaken in order to find the optimum condition of the preparation of the sensitive and stable surface of the copper-beryllium target suitable for the secondary electron multiplier. This paper reports the main results of the following studies:

(1) the dependency of the electron yield of the non-activated and activated target surfaces upon the kinetic energy of various noble gas and hydrocarbon ions;

(2) the determination of the surface structures of the ion targets by means of electron diffraction analysis; and

(3) the influence of the temperature of treatment upon the electron yield and the stability of the target surfaces.

Experimental

Mass Analyser and Ion Targets. — The present experiments were performed by a mass spectrometer self-constructed in our laboratory. This mass spectrometer is a single focusing 90° sector type and the radius of curvature of the ion path is 135 mm., and the ion source of the usual electron bombardment type was installed in this instrument. In the present experiments two kinds of simple detectors were used. The constructions of the target assembly of them are schematically shown in Figs. 1a and 1b.

In Fig. 1a, T_1 indicates the ion target, C_1 the collecting plate of secondary electrons, S_1 the enclosing cage of the detector, and E_1 the collector slit. The other detector shown in Fig. 1b was constructed in order to measure the electron yield of the copper-beryllium surface by the bombardment of secondary electrons. But in the present experiments this detector shown in Fig. 1b was also used for the measurements of the electron yield by the bombardment of various positive ions. In Fig. 1b, T_2 indicates the ion traget, **D** and C_2 the collecting plates of sencondary electrons, S_2 the enclosing cage of the detector, E_2 the collector slit.

The geometries of the ion tragets (T_1 and T_2) and the collecting plate of secondary electrons (**D**) are similar to those of the electron multiplier of the Nier type[7]. The width of the collector slit was fixed to 2 mm., while the width of the exit slit of

1) M. G. Inghram, "Mass Spectroscopy in Physical Research", NBS Circular No. 522, 257 (1953).
2) M. G. Inghram, "A Handbook on Mass Spectroscopy", National Academy Sciences (1954), p. 41.
3) H. D. Hagstrum, *Phys. Rev.* **89**, 244 (1953).
4) H. D. Hagstrum, ibid., **91**, 543 (1953).
5) H. D. Hagstrum, ibid., **96**, 325, 336 (1954).
6) H. D. Hagstrum, ibid., **104**, 317, 672, 1516 (1956).
7) K. S. Quisenberry, T. T. Scolman and A. O. Nier, ibid., **102**, 1071 (1956), W. H. Johnson, Jr. and A. O. Nier, ibid., **105**, 1014 (1957).

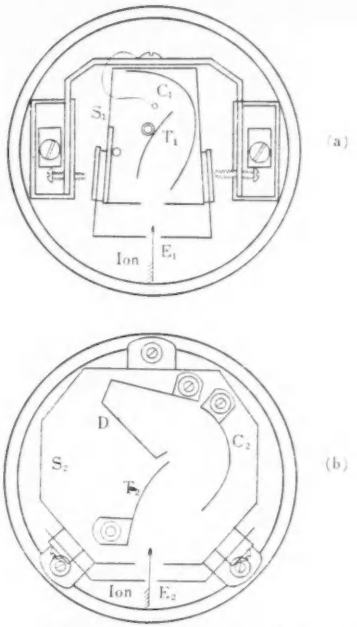

Fig. 1. Schematic diagrams of the ion collectors of the mass spectrometer. T_1(a) and T_2(b) are the ion targets, C_1 (a) and D(b) are the electron collectors, C_2(b) is Cu-Be dynode, S_1(a) and S_2(b) are the enclosing cages, and E_1(a) and E_2(b) are the collector slits.

the ion source is 0.2 mm. The ion targets were formed from the copper-beryllium plates* of 0.16 mm. in thickness, and the collecting plates of secondary electrons, the enclosing cages and the collector slits were all shaped from the molybdenum plates of 0.15 mm. in thickness.

For the measurements of the ion currents the collector slit (E_1 or E_2) and the ion target (T_1 or T_2) were kept to the earth potential and the electron suppressor voltage of -20 V. was supplied to all collecting plates (C_1 and S_1 in Fig. 1a; D, C_2 and S_2 in Fig. 1b). On the other hand, for the measurements of the secondary electron currents the collecting plates of secondary electrons were all kept to the earth potential and the potential of -270 V. was supplied to the ion target. It has been experimentally confirmed that these two types of detectors show the same value in the electron yield under the same experimental conditions.

A UX-54 tube was used as the primary tube of the d. c. amplifier, and the output currents were recorded by two galvanometers that have different sensitivities. The end vacuum under the ordinary experimental conditions was somewhat better than 1×10^{-6} mm Hg.

Treatment of Ion Targets. — The non-activated targets were treated in the following manner. After being tempered, the alloy plates were mechanically polished with the fine emery papers of No. 0000 to 0005. After that the ion targets were formed and then electropolished in the polishing solution** for about one minute.

The treatment of activation of the ion targets was carried out in a quartz tube (25 mm. in outer diameter and 300 mm. in length) which was connected by the water-cooled taper joint to the vacuum system, the reservoir of purified oxygen and a McLeod gauge. The quartz tube was heated in an electric furnace and the temperature was measured by a copper-constantan thermocouple enclosed in this quartz tube. The electropolished targets were put into the quartz tube and evacuated to lower than 5×10^{-6} mmHg at about 800°C for three hours. After the evacuation the temperature was lowered to each required temperature (i. e. 350, 420, or 480°C), and then the known quantity of oxygen was introduced into the quartz tube. The initial pressure of oxygen for each treatment was about 2×10^{-2} mmHg, and the pressure decrease in each time was measured by a McLeod gauge.

The results are shown in Fig. 2. As seen in

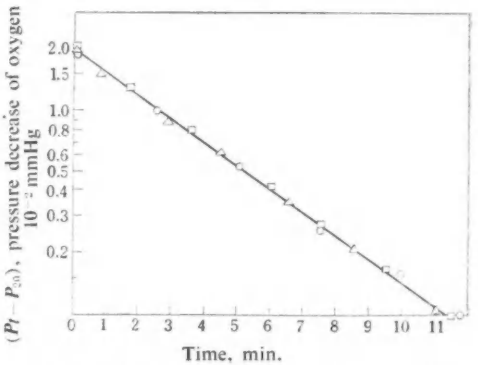

Fig. 2. Rate of the pressure decrease of the oxygen, by the treatment of the Cu-Be at the various temperatures: □; 350°C, △; 420°C and ○; 480°C.

Fig. 2, the present results indicate that the initial rate of the pressure decrease is independent of the temperature of treatment. After the treatment of 20 min. the quartz tube was evacuated and gradually cooled to the room temperature, and then the targets were taken out and mounted in the ion collector of the mass spectrometer.

Determination of Surface Structure. — The surface structure of the non-activated and activated ion targets was analysed by means of a commercial Hitachi E. D. C. type electron diffraction apparatus.

Gaseous Materials. — Oxygen was prepared by the thermal decomposition of potassium permanganate, and purified by passing through the trap

* The copper-beryllium plates of 0.16 mm. in thickness were prepared from a copper-beryllium(4%) alloy rod of the Beryllico Co., U. S. A.

** The electropolishing solution was prepared by mixing four volumes of phosphoric acid, four volumes of glycerin and three volumes of water.

cooled by liquid nitrogen. Spectroscopically pure argon and neon of the Teikoku Oxygen Co. were used without any further purification. The mass spectrometric analyses of these gaseous samples revealed that the total impurities were less than 0.005 per cent in volume. The research grade ethylene and ethane of the Philips Petroleum Co. were used in the present experiments, and the purity was also checked by means of the mass spectrometer.

Results

Surface Structure of Copper-Beryllium Targets. — The surface structures of the copper-beryllium targets examined by the electron diffraction apparatus are summarized in Tables I and II. The main results of the analysed interplanar distances for the three kinds of ion targets — i. e. (a) tempered at about 800°C and mechanically polished, (b) tempered, mechanically polished, and then electropolished, and (c) tempered, mechanically polished, electropolished, and then bombarded by various positive ions for five hours — are listed in Table I together with that of Cu, Cu_2O and CuO by X-ray diffraction analysis[8] for the sake of comparison. As seen in Table I, the oxide films of copper (mainly Cu_2O) are partially left on the mechanically polished surface (a). The electropolished surface (b) shows that the mechanically polished surface was re-oxidized by electropolishing, while the surface bombarded by various positive ions (c) indicates that the electropolished surface was partially reduced during the prolonged bombardments of various positive ions.

TABLE I. INTERPLANAR SPACINGS (Å) OF Cu-Be SURFACES MEASURED BY ELECTRON DIFFRACTION

(1) NOT TREATED SURFACES

(a) Mechanical polished surface, (b) electropolished surface, (c) after ion irradiation of the electropolished surface, and included the X-ray data of Cu, Cu_2O and CuO.

(a)	(b)	(c)	Cu	Cu_2O	CuO
2.998	2.301	2.992	2.08	3.00	2.51
2.443	2.166	2.623	1.81	2.45	2.21
2.207	1.758	2.395	1.277	2.12	1.70
2.010	1.522	2.180	1.228	1.51	1.57
1.816	1.273	1.766	1.089	1.283	1.50
1.540	1.131	1.649	1.043	1.065	1.408
1.356	0.956	1.577	0.905	0.971	1.370
1.235	0.874	1.176		0.869	1.254
1.155				0.819	1.159
1.070					1.086
1.030					1.007
0.864					0.855

8) K. Kubo, "The Method of Chemical Analysis by Meanes of X-ray Diffraction", Shukyosha Co., Tokyo (1947), pp. 118, 152, 156.

TABLE II. INTERPLANAR SPACINGS (Å) OF Cu-Be SURFACES MEASURED BY ELECTRON DIFFRACTION

(2) TREATED SURFACES BY OXYGEN

Included the X-ray data of BeO and CuO.

Treated temperature			BeO	CuO
480°C	420°C	350°C		
2.477	2.470	2.476	2.34	2.51
2.283	2.317	2.290	2.19	2.31
2.218	2.161	2.172	2.06	1.85
2.096	1.993	2.031	1.59	1.70
2.001	1.565	1.497	1.350	1.57
1.808	1.523	1.313	1.239	1.50
1.566	1.315	1.272	1.170	1.408
1.429	1.200	1.217	1.150	1.37
1.312	1.124	1.174	1.130	1.298
1.275	1.060	1.123	1.032	1.254
1.171	0.919	1.057	0.915	1.159
1.163	0.888	1.036	0.884	1.086
1.123	0.855	0.969	0·870	1.007
1.074	0.796	0.863	0.822	0.978
1.053	0.753	0.796	0.780	0.885
1.038		0.741	0.758	
0.975				
0.874				
0.849				
0.789				
0.758				

The interplanar distances analysed for the activated surfaces treated at various temperatures are summarized in Table II together with the X-ray diffraction data[8] of BeO and CuO. As seen in Table II, the difference in the surface structure between each temperature of the treatment is not clear, but the diffraction patterns peculiar to BeO are clearly observed for all specimens. This fact may be interpreted to mean that beryllium ions (or atoms) in the alloy rapidly migrate through the lattice and arrive at the surface at these temperatures of the treatment, and that since they easily react with oxygen and are fixed as beryllium oxide the concentration of this compound in the neighborhood of the alloy surface will be considerably increased by the treatments of activation.

Dependency of Electron Yield upon Ion Kinetic Energy. — In Figs. 3 and 4, the electron yield for the non-activated and activated (treated at 420°C) target surfaces is plotted as a function of the kinetic energy of singly- and doubly-charged argon ions and the five different ions from ethylene, respectively. The variation of the electron yield with the kinetic energy of the parent and fragment ions from ethane for the activated target surface treated at 420°C is shown in Fig. 5. Fig. 6. shows

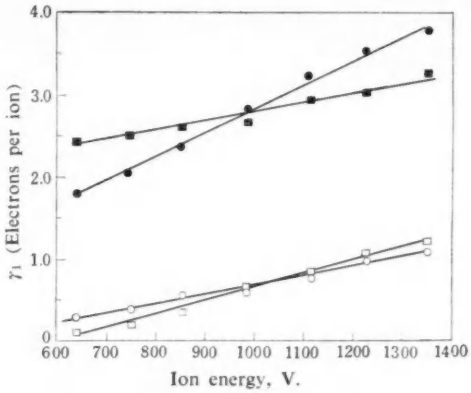

Fig. 3. Plot of experimental data giving electron yield γ_i, as a function of ion kinetic energy for A^+(● activated, and ○ non-activated) and A^{2+}(■ activated and □ non-activated) on 420°C activated and non-activated Cu-Be targets.

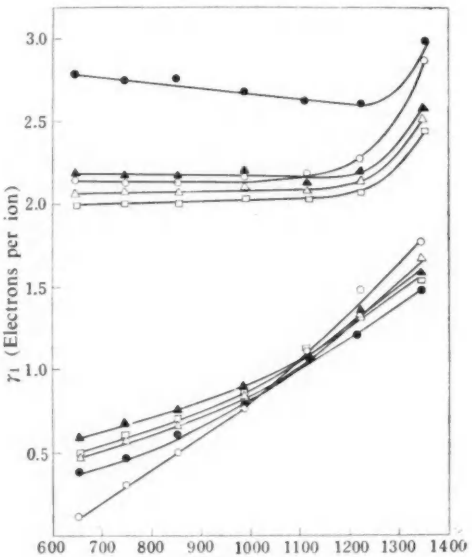

Fig. 4. Plot of experimental data giving electron yield γ_i, as a function of ion kinetic energy for parent and fragment ethylene ions; upper five curves are data on the 420°C activated Cu-Be target and lower are data on the non-activated Cu-Be target. ○; $C_2H_4^+$, △; $C_2H_3^+$, □; $C_2H_2^+$, ▲; C_2H^+, and ●; C_2^+.

the influence of the temperature of the treatment (480, 420 and 350°C) on the variation of the electron yield with the kinetic energy of singly- and doubly-charged neon ions.

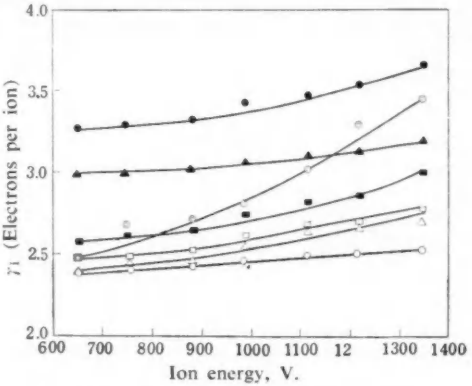

Fig. 5. Plot of experimental data giving electron yield γ_i, as a function of ion kinetic energy for parent and fragment ethane ions: ○; $C_2H_6^+$, ■; $C_2H_5^+$, ○; $C_2H_4^+$, △; $C_2H_3^+$, □; $C_2H_2^+$, ▲; C_2H^+, and ●; C_2^+, on activated target treated at 420°C.

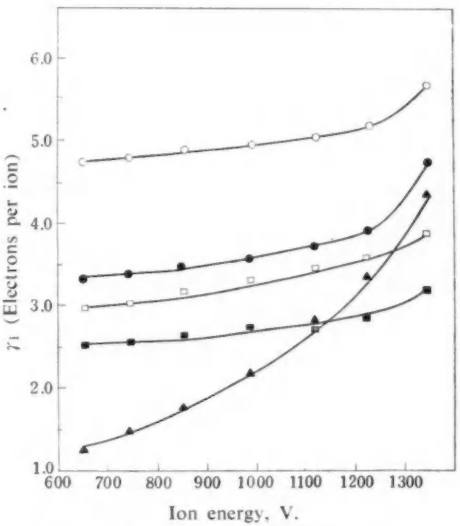

Fig. 6. Plot of experimental data giving electron yield γ_i, as a function of ion kinetic energy for singly- and doubly-neon ions on activated target treated at various temperatures.
○; Ne^{2+}, 420°C, ●; Ne^+, 420°C, □; Ne^{2+}, 350°C, ■; Ne^+, 350°C, ▲; Ne^+, 480°C.

Stability of Electron Yield by Ion Impacts. —Under the present experimental conditions, the electron yield for the non-activated surface gradually decreased and reached about 80 per cent of its initial value by the prolonged

TABLE III. THE SECONDARY ELECTRON YIELDS (γ_1) AND THE IONIZATION POTENTIALS (I. P.) AND THE APPEARANCE POTENTIALS (A. P.)

The values of γ_1 are shown for 980 volts ion energy and for the target surface activated at 420°C.

Ion	Ethane			Ethylene		
	I. P.[9] eV.	γ_1 electrons/ion	A. P.[9] eV.	γ_1 electrons/ion	A. P.[9] eV.
$C_2H_6^+$	11.6	2.75	11.6	—	—
$C_2H_5^+$	8.7	2.90	12.9	—	—
$C_2H_4^+$	10.8	2.50	12.1	2.20	10.8
$C_2H_3^+$	9.9	2.55	15.2	2.09	14.1
$C_2H_2^+$	11.2	2.50	15.0	2.04	13.4
C_2H^+	11.3	3.05	27.0	2.20	19.2
C_2^+	—	3.05	31.5	2.70	26.4

bombardments of the various positive ions mentioned above for five hours. On the other hand, no measurable decrease in the electron yield for the activated target surface treated at 420°C was obtained within the limit of the experimental errors by the prolonged bombardments of various ions for ten hours.

Discussion

As seen in Figs. 3 and 4, the electron yield of the activated surface treated at 420°C for the argon ions or the various ions of ethylene is considerably larger and more stable than that of the non-activated surface. Moreover, as seen in Figs. 3—6 (excepting the results obtained for the activated surface at 480°C in Fig. 6), the increment of the electron yield for each activated surface with the kinetic energy of various ions in the range 600 to 1000 V. is very small, while that for the non-activated surface in the same energy range is considerably large. The typical results shown in Fig. 6 indicate that the electron yield and the increment of it with the kinetic energy of ions are greatly influenced by the temperature of the treatment. It is worth while to notice that the electron yield curve of the singly-charged neon ions for the target surface activated at 480°C is markedly different from those activated at 350 and 420°C.

These characteristics in the electron yield of the activated target surfaces might be correlated with the structure and the concentration of beryllium oxide formed in the neighborhood of the target surface. But unfortunately, the present results of the electron diffraction analyses shown in Tables I and II can not elucidate the fine structures of the oxide layers, and the more detailed measurements of the surface structure are necessary in order to discuss the correlation mentioned above.

The detailed experiments and theoretical treatise on the mechanism of the electron ejection by the impacts of various noble gas ions from both atomically clean surfaces of molybdenum and tungsten and the surfaces of tungsten covered by various foreign gases have been reported by Hagstrum[5,6]. From his results it has been suggested that the probability of the electron ejection in a non-Auger process may begin at low ion energies when a monolayer is present on the target surface and that even for the atomically clean surface there is strong evidence of a non-Auger process setting in at energies above 400 eV. with the singly-charged helium ions.

The present results shown in Figs. 3—6 indicate that the electron yield for the activated surface of copper-beryllium by various noble gas and hydrocarbon ions is only slightly influenced by the kinetic energy of ions, while for the non-activated target surface there is a marked increase in the electron yield with the increase in the ion kinetic energy. But since we must recall that under the present experimental conditions the considerable part of the target surface might be covered by the residual gases, it seems unreasonable to simply correlate the mechanism of the electron ejection from the activated and non-activated surfaces to the Auger and a non-Auger processes, respectively.

Hagstrum[3] also reported that when the electron ejection from the target surface is mainly dominated by the Auger neutralization process the electron yield is proportional to the value of the ionization potential minus twice the work functions of the target surface. The present results of the electron yield for the target surface activated at 420°C and the literature values[9] of the ionization potentials are summarized in Table III. When we assume that the electron ejection from the activated target surface of copper-beryllium simply obeys the Auger neutralization process and that the work function was unchanged throughout the

9) G. C. Eltenton, *J. Chem. Phys.*, **15**, 455 (1947).

measurements, it is reasonable to expect that the electron yield is proportional to the ionization potential. Table III indicates that the present results are somewhat complicated and do not simply satisfy the proportionality mentioned above.

Since the present experimental conditions are considerably complicated, it is necessary to continue more detailed experiments on the dependency of the electron yield upon the ion energy and energy distribution of secondary electrons both for the activated and non-activated target surfaces which are atomically clean and covered by foreign gases in order to discuss the mechanism of the electron ejection process.

Summary

The secondary electron emission from the non-activated and activated surfaces of copper-beryllium (4%) by the impacts of various noble gas and hydrocarbon ions was studied together with the determination of the surface structure by the electron diffraction analysis. The main results obtained are as follows.

(1) The considerably thick layer of beryllium oxide is formed in the neighborhood of the target surface activated by oxygen at the temperature range of 350 to 480°C.

(2) The oxide films of copper are formed on the target surface by electropolishing, but these oxides easily undergo reduction by the prolonged ion bombardments.

(3) The optimum temperature of activation for the electron yield seems to be about 420°C, and the electron yield for the activated target surface treated at 350 or 420°C is only slightly dependent upon the ion kinetic energy.

(4) No measurable decrease in the electron yield for the activated surface treated at 420°C was obtained by the prolonged bombardments of various positive ions for ten hours, while the electron yield for the non-activated surface decrease about 20 per cent by the prolonged bombardments of ions for five hours.

(5) Under the present experimental conditions, the mechanism of the electron ejection process seems to be considerably complicated and it is difficult to deduce any definite conclusion for the electron ejection process.

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Inorganic Extraction Studies on the System between Bis(2-ethyl hexyl)-orthophosphoric Acid and Hydrochloric Acid. II

By Kan KIMURA

(Received July 25, 1960)

In the previous paper[1], was reported the influence of acid concentration on the solvent extraction of about fifty elements in the system of 50 percent bis(2-ethyl hexyl) orthophosphoric acid (HDEHP)-aqueous hydrochloric acid. As is well known in solvent extraction studies[2], the distribution ratio, K_d, is much affected by the solvent concentration in a way similar to that by the acid concentration.

Accordingly, a study on the influence of solvent concentration in organic phase is very important for the purpose of determining the suitable concentration for a given separation procedure. Besides that, the relationship

1) K. Kimura, This Bulletin, 33, 1038 (1960).
2) G. H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry", John Wiley & Sons Inc., New York (1957), p. 52.

between K_d values of a given ion and solvent concentrations gives some suggestions on the chemistry of the extraction.

Along this line, have been published many studies[3-5] on the chemical mechanisms of thenoyltrifluoroacetone extraction or the chemical composition of the thenoyltrifluoroacetates. Concerning HDEHP extraction, the solvent dependence of the distribution ratios was already studied for lanthanide elements[6-8], uranium[8-9], iron and a few other chemical elements[8]. However, no comprehensive study on the extraction from a given mineral acid solution has been reported. In the present paper, the influence of solvent concentration is presented, discussing the extraction carried out from hydrochloric acid solution of a given acidity containing each of about fifty elements.

Experimental

Sources of Materials. — The bis(2-ethyl hexyl)-orthophosphoric acid received from Virginia Chemicals Co. was purified and checked on its purity as reported in the previous study[1]. The work reported here was carried out using HDEHP diluted with toluene of guaranteed reagent grade.

Radioisotopes used were the same as those which were reported previously[1] except for the following: The nuclides 19day ^{86}Rb and 40day ^{103}Ru were imported and used as received. The radioactive tracers of neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium and lutetium contributed for counting were mainly 11.3day ^{147}Nd, 47 hr. ^{153}Sm, 9.2hr. ^{152}Eu, 18.0hr. ^{159}Gd, 73day ^{160}Tb, 2.32hr. ^{165}Dy, 9.4day ^{169}Er, 129day ^{170}Tm and 6.8day ^{177}Lu, respectively[10]. These were prepared by the neutron irradiation of highly-purified oxides in JRR-1. In the cases of gadolinium and erbium, the radioactivities caused by the radioactive daughters (6.75day ^{161}Tb and 680day ^{171}Tm) of simultaneously yielded short half-lived nuclides (3.73 min. ^{161}Gd and 7.5hr. ^{171}Er) were corrected from the total activities of gadolinium and erbium by the results of their decay measurements, respectively. The nuclide 27.4day ^{233}Pa was obtained as a by-product of uranium-233 processings[11].

The radiochemical purity of these nuclides was checked by their half-lives, γ-ray spectra, and/or β-ray absorption curves with aluminum foils.

Determination of Distribution Ratios.—The distribution ratio, K_d, of a given nuclide was radiometrically determined. The details and some remarks of the method written about in the previous report[1] were also adopted in the present study. Most of the data in this experiment were obtained after shaking the two layers for three minutes.

Although the HDEHP concentration in the organic layer was varied usually in the range from 0.5 to 50 volume percent, it was extended to 0.01 volume percent in some cases. The extraction with barren toluene containing no HDEHP was also checked. On the other hand the acidity in the aqueous layer was kept constant in a series of extractions of a given element.

Results and Discussion

The results are summarised in Fig. 1 as a series of graphs of $\log K_d$ vs. $\log$ (% HDEHP) where K_d is the distribution ratio and % HDEHP the concentration of HDEHP in volume percentage.

As reported previously[1], K_d values for each cation usually depend on inverse power of hydrogen ion concentration, and furthermore K_d values for mono-, di-, tri-, and tetra-valent cation decrease with the following general sequence; $M^{4+} > M^{3+} > M^{2+} > M^{+}$. Meanwhile, K_d values for the ion ready to form an anion are usually low. Therefore, it is desired that the acidity should be changed according to the valence of the ion concerned.

Although the acidity of aqueous phase was kept constant at 0.5 N for most of the elements, it was 0.05 N for the alkali and alkaline earth elements, 0.3 N for the rare earth elements, and 0.1 N or 2 N for some other elements. In some cases, the extractions of ion from the solutions of two different acidities were undertaken. The Arabic numeral in each graph shows the acidity taken.

Fig. 1 was compiled from some published and unpublished results. Data for lead and bismuth were taken from the observation of Ishimori[12]. Data for yttrium, promethium, thulium and americium were taken from the work of Peppard et al[6]. The K_d values for selected lanthanide cation(III) in HDEHP-hydrochioric acid system are inverse third power dependent on the hydrogen ion concentration of the aqueous phase. Therefore, K_d values for yttrium, promethium, thulium and americium were obtained correcting Peppard's value (at 0.552 M, 0.146 M, 0.552 M, and 0.275 M, respectively) for 0.3 N hydrochloric acid solution.

As is seen in Fig. 1, the K_d values for each

3) R. E. Connick and W. H. McVey, *J. Am. Chem. Soc.*, **71**, 3128 (1949).
4) E. H. Hyffman and L. J. Beaufait, ibid., **71**, 3179 (1949).
5) J. C. Sullivan and J. C. Hindman, ibid., **76**, 5931 (1954).
6) D. F. Peppard, G. W. Mason, J. L. Maier and W. J. Driscoll, *J. Inorg. Nucl. Chem.*, **4**, 334 (1957).
7) D. F. Peppard, G. W. Mason, W. J. Driscoll and R. J. Sironen, ibid, **7**, 276 (1958).
8) C. A. Blake, Jr., C. F. Baes, Jr., K. B. Brown, C. F. Coleman and J. C. White, "Proceedings of the International Conference on the Peaceful Uses of Atomic Energy", Vol. 28, United Nations, Geneva (1958), p. 289.
9) C. F. Baes, Jr., R. A. Zingaro and C. F. Coleman, *J. Phys. Chem.* **62**, 129 (1958).
10) K. Kimura, "Hoshasen Data Book", Chijin Shokan, Tokyo (1958) p. 92.
11) T. Ishimori et al., unpublished.
12) T. Ishimori, unpublished.

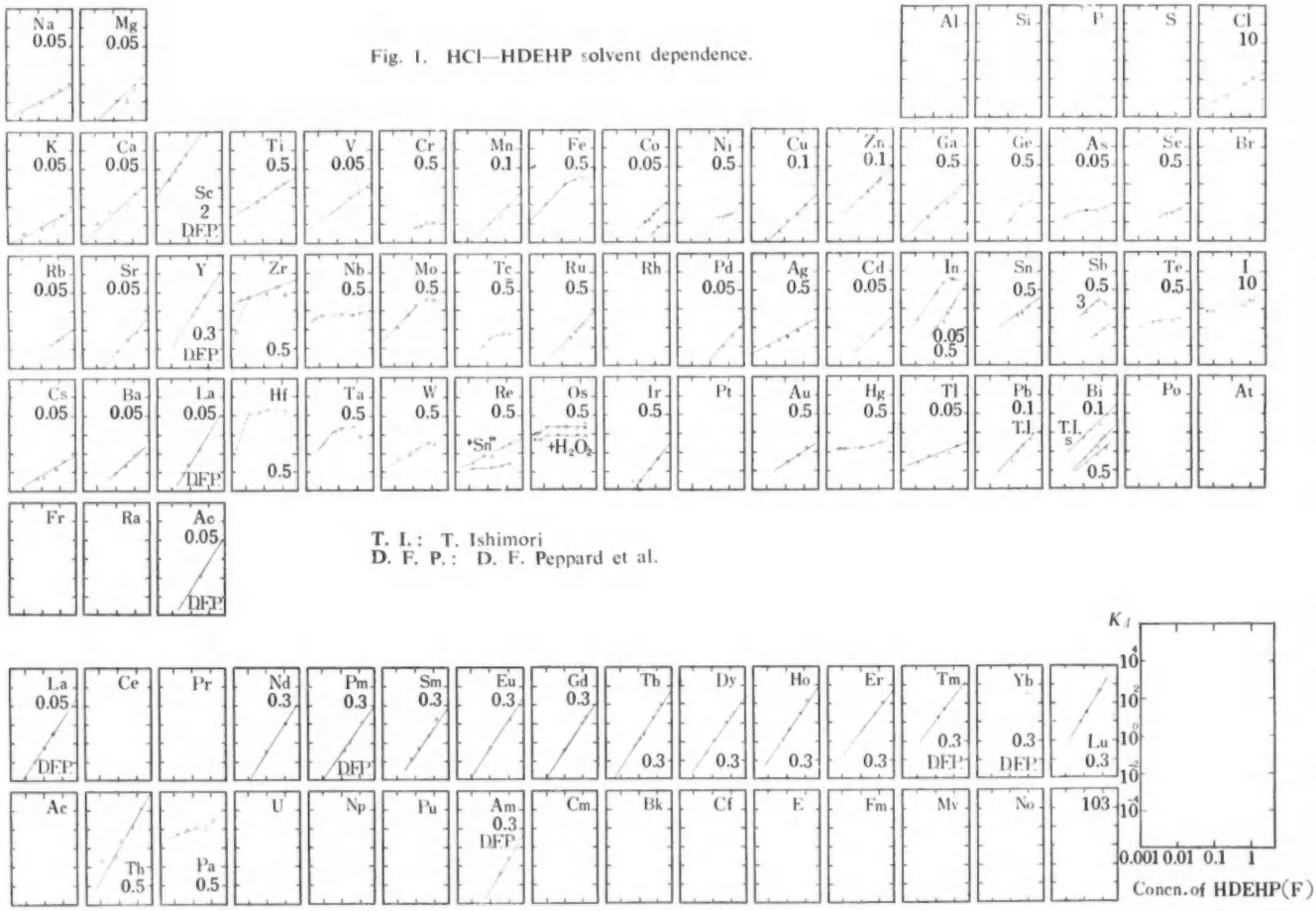

Fig. 1. HCl—HDEHP solvent dependence.

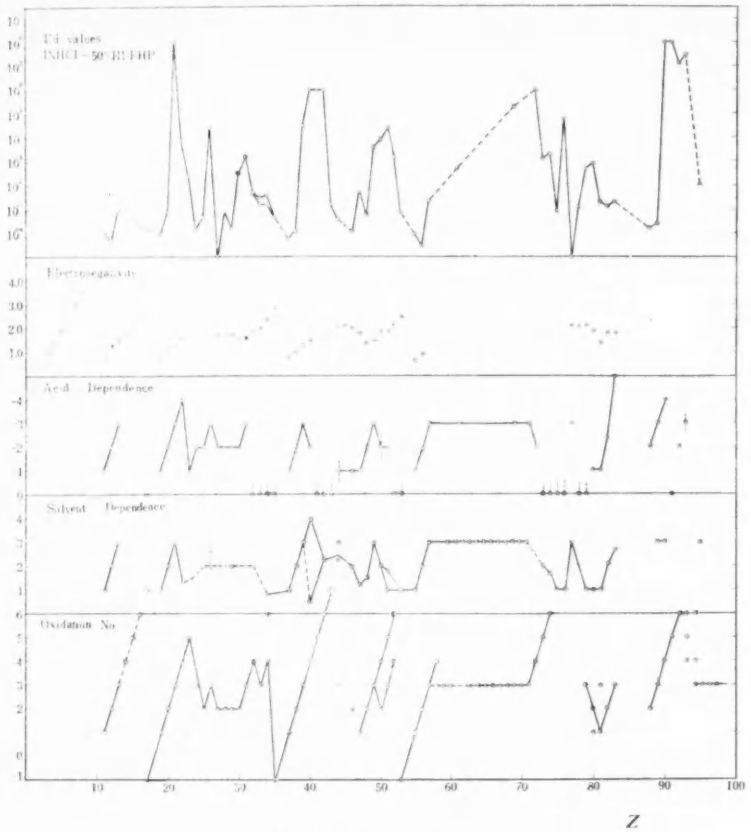

Fig. 2. Z dependences.

of almost all the elements increase as the concentration of HDEHP in the toluene phase increases. A similar relationship is observed generally in many solvent extraction systems.

The K_d values for alkali metals, alkaline earth metals and lanthanide elements show the first, second and third power dependence on the HDEHP concentration in the toluene phase, respectively. A similar relationship holds for some other elements: silver and thallium(I) indicate the first power solvent dependence, manganese, cobalt, copper, zinc and cadmium the second dependence, and indium indicates the third. The K_d values for iron and gallium follow the second power solvent dependence and those for thorium the third dependence.

The K_d values for zirconium remain nearly constant in almost the whole range of the solvent concentration. Although the strange behavior of zirconium is not clearly explained, it might be caused by both the hydrolysis of zirconium ion and its high K_d values. Scadden and Ballou[13] reported that only zirconium and indium are completely extracted with 0.06 M dibutylphosphoric acid (HDBP) for 1 M nitric, hydrochloric, or perchloric acid; and Ishimori et al[14] reported that only zirconium is extracted with dilute tributyl phosphate (1%, toluene diluent) from 8 M hydrochloric acid solution of the fission products. Furthermore, White[15] reported that zirconium is completely extractable from 1 M hydrochloric acid solution with 0.1 M trioctylphosphine oxide and partially extractable with 0.1 M tris-2-ethylhexyl phosphine oxide. This high extractability of zirconium with many alkyl phosphorous reagents is noteworthy as compared with the very low solubility of zirconium phosphate in mineral acids. Hafnium, niobium and protactinium resemble zirconium in the solvent dependence of their K_d values.

13) E. M. Scadden and N. E. Ballou, *Anal. Chem.*, 25, 1602 (1953).
14) T. Ishimori K. Umezawa and K. Watanabe, *J. Atomic Energy Soc. Japan* **1**, 299 (1955).
15) J. C. White, USAEC TID-7555, 249 (1958).

The K_d values for osmium are relatively high and kept nearly constant. Besides that, osmium can be extracted with pure toluene fairly well, giving the K_d value of 1.31. This K_d value is as low as about one tenth of the K_d values for toluene containing HDEHP. The K_d value is shown with open circles attached with arrow in Fig. 1. The addition of hydrogen peroxide to the tracer solution makes all the K_d values for osmium low, keeping the shape of the curve unchanged. This would be explained as a partial reduction of the readily extractable species of osmium. Thus, the relatively high K_d values for osmium might be explained assuming the extraction of a neutral molecule such as osmium tetroxide. Futhermore, the higher K_d values with the HDEHP toluene solution might indicate that HDEHP promotes the extraction to some extent.

The K_d value for mercury with pure toluene is also high. It appears as if the extraction of mercury is partially based on the extraction of a neutral molecule such as $HgCl_2$, which is slightly ionized in the low concentration region of chloride.

In the case of iodine, the K_d values for the acid range up to 5 N were very low[12]. However, the slightly high K_d value is obtained at 10 N. Similarly the K_d value for pure toluene at 10 N hydrochloric acid remains high. It may be based on the oxidation of tracer quantity of iodide ion with the micro-amount of chlorine. Scadden and Ballou[13] reported that the neutral iodine molecule, I_2, showed a high extractability with dibutyl phosphate.

The different slopes of solvent dependence curve for bismuth are obtained varying the acid concentration of aqueous phase. Because it is known that bismuth forms a series of chloride complexes in hydrochloric acid solution[16], and that the ratios among these chloride complexes vary with the chloride concentration, it may be natural that the slope is changed according to the acid concentration.

On the other hand, the slopes of the K_d curves for indium and rare earth elements are not dependent on the acid concentration. For instanse, the K_d values for thulium follow the third power solvent dependence both at 0.552 M[7] and at 0.3 N hydrochloric acid. Concerning the K_d values for indium, a similar relationship also holds at 0.5 N and 0.05 N hydrochloric acid. The K_d values for cobalt are very low, but similar results are obtained at 0.5 N and 0.05 N, using a larger amount of radioactive cobalt-60.

The slopes of the solvent dependence and of the acid dependence and the oxidation number are plotted against the atomic number, Z, in Fig. 2. The graph of the "best values of electronegativity"[17] vs. Z and that of the K_d values between 50% HDEHP and 1 N hydrochloric acid vs. Z are attached to Fig. 2. The values of electronegativity of cobalt, nickel, ruthenium, rhodium, palladium, iridium and platinum are taken from Haïsinsky's data[18].

As mentioned above, the solvent dependence is studied at one of the several definite acidities. Accordingly the data of the solvent dependence may not be suitable for detailed discussion, because the formation of chloro-complexes differs both with the acidity and with the element. However, the data may be applicable to general discussion. The vertical dotted lines indicate that the slope could not be clearly obtained. Almost all of the elements showed the slope defined as "the second type" in the previous paper indicate the slope of zero in the graph of the acid dependence vs. Z.

As is seen in Fig. 2, the slopes and the oxidation numbers vary regularly in Na–Mg–(Al), K–Ca–Sc, Rb–Sr–Y, and Cs–Ba–La, showing the increasing lines with increasing Z. Although the Fr–Ra–Ac–line is not studied, it may follow the similar relationship. Concerning the Ib–IIb–IIIb group of the periodic table, only the Ag–Cd–In line is satisfied with this increasing relation. On the other hand, the Cr–Zn line or La–Lu line is nearly horizontal. The curves indicate some complicated relationships for the ranges of the IVb–Vb–VIb group and of the platinum group in the periodic table.

Fig. 2 shows that the relation among the slopes of the dependences and the oxidation number is roughly divided into two types.

The first type is characteristic in the fact that the relation which the slope of the solvent dependence has equals that of the acid dependence and further that the oxidation number does so also. Scandium, yttrium, or lanthanum are satisfied with this relationship. This tendency is generally observed in the solvent extraction system where chelation plays an important role:

$$M^{m+}_{(aq.)} + mHR_{(org.)} \rightleftarrows MR_{m(org.)} + mH^{+}_{(aq.)} \quad (1)$$

In Eq. 1, the distributio ration of M is given:

$$K_d = K[HR]^{m}_{(org.)}[H^{+}]^{-m}_{(aq.)} \quad (2)$$

Baes and Peppard[6,7] assumed the following

16) L. S. Newman and D. N. Hume, *J. Am. Chem. Soc.*, 79, 4576 (1957).

17) H. O. Pritchard and H. A. Skinner, *Chem. Revs.* 55, 767 (1955).

18) M. Haïsinsky, *J. Phys.* 7, 7 (1946); *J. Chim. Phys.* 46, 298 (1949).

equilibrium for the reaction between uranium(VI) or lanthanide elements in perchloric acid solution and HDEHP, considering that the HDEHP molecule is essentially completely dimerized in the toluene phase:

$$M^{m+}_{(aq.)} + m(HDEHP)_{2\,(org.)} \rightleftarrows MH_m(DEHP)_{2m(org.)} + mH^+_{(aq.)} \quad (3)$$

where the K_d value of M is given as:

$$K_d = K[(HDEHP)_{2(org.)}]^m [H]^{-m}_{(aq.)} \quad (4)$$

It is assumed that the alkali metal cation(I) and the alkaline earth metal cations(II) follow Eq. 3, showing the first and second power solvent dependence and the inverse first and second power acid dependence, respectively. Because manganese(II), cobalt(II), copper(II), zinc(II), silver(I), cadmium(II), indium(III) and thallium(I) also show the relationship of equal figures, it seems that they are also satisfied with Eq. 3.

K_d values of iron(III) are approximately second-power dependent on the HDEHP concentration for 0.5~0.05% HDEHP in the organic phase and are inverse third-power dependent on the acid concentration in the aqueous phase. Thus, iron belongs to a modified first type. Blake et al.[8] postulate the following equilibrium for the partition of ferric iron:

$$Fe^{3+} + 2(HDEHP)_2 + HOH \rightleftarrows Fe(OH)H_2(DEHP)_4 + 3H^+ \quad (5)$$

Besides that, Peppard and Ferraro[19] mentioned that the solvent extraction of thorium is approximately third-power dependent on the HDEHP concentration and inverse forth-power dependent on the HDEHP concentration and inverse forth-power dependent on the acid concentration, and that these tentative dependencies are consistent with either or both of the following equilibria:

$$M^{4+}_{(aq.)} + 3H_2DEHP_{2\,(org.)} \rightleftarrows MDEHP_2(HDEHP_2)_{2\,(org.)} + 4H^+_{(aq.)} \quad (6)$$

and

$$M^{4+}_{(aq.)} + 3H_2DEHP_{2\,(org.)} + HOH \rightleftarrows M(OH)(HDEHP_2)_{3\,(org.)} + 4H^+_{(aq.)} \quad (7)$$

It seems that the solvent extraction of gallium also follows similar equilibria, showing the second-power solvent dependence and the inverse third-power acid dependence. A similar relationship also holds for the extraction of titanium.

On the other hand, the second type is characteristic both in the acid dependence with the slope of zero defined as "the second type"[1] and in the solvent dependence with the slope of one or more. These tendencies are commonly seen in the solvent extraction, in which the ion association plays an important role[20] such as TBP extraction of uranyl ion[21].

Chlorine, selenium, molybdenum, tungsten and gold, which form anions easily and have a relatively high value of electronegativity, are typical for the second type. Accordingly, it appears that the solvent extraction of these elements is based on partition as is found in the extraction with TBP. As for the electonegativity, it is noticed that the more extractable element generally has a value between 1.0 and 2.0.

Thanks are due to Dr. Tomitaro Ishimori for his guidance and suggestions, to Dr. Kenjiro Kimura and Dr. Toshio Nagai for their encouragement, and also to Mr. Ikuo Suzuki for his assistance.

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19) D. F. Peppard and J. R. Ferraro, *J. Inorg. Nucl. Chem.*, **10**, 275 (1959).

20) G. H. Morrison and H. Freiser, Ref. 2, p. 59.

21) K. Naito, This Bulletin, **33**, 363 (1960).

Studies on Antibiotics and Related Substances. XI. Methylated Amino-sugar Moieties from Methylated Kanamycin[1]

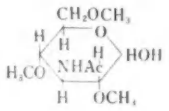
By Sumio UMEZAWA and Yukio ITŌ

(Received July 25, 1960)

In a previous paper[2] we described the fact that 1, 3-diamino-4, 6-dihydroxy-5-methoxycyclohexane was isolated from the hydrolyzate of exhaustively methylated *N*-acetyl kanamycin. It was therefore concluded that both of the two aminohexose moieties in kanamycin are directly joined to deoxystreptamine through 4- and 6-hydroxyl groups by glucosidic linkages, the structure of kanamycin[3] being established. Subsequently, attempts have been made to isolate amino-sugar moieties from the same hydrolyzate. The present paper is concerned with the isolation of methylated derivatives of 3-amino-3-deoxy glucose and 6-amino-6-deoxyglucose.

Separation of 1, 3-diamino-4, 6-dihydroxy-5-methoxycyclohexane from acid-hydrolyzate was accomplished as described in a previous paper[2]. The residue from the mother liquor was chromatographed on a column of cellulose powder with butanol–ethanol–water (4 : 1 : 5). Repetition of the chromatography resulted in the isolation of 3-acetamido-3-deoxy-2, 4, 6-tri-*O*-methyl-D-glucose (I). The new derivative was converted into a methyl glucoside, which has been identified with the synthetic specimen prepared from D-glucose by the route of Peat and Wiggins[4].

On the other hand, an aqueous solution of



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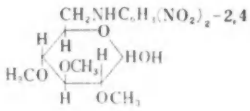
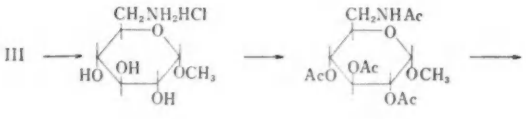


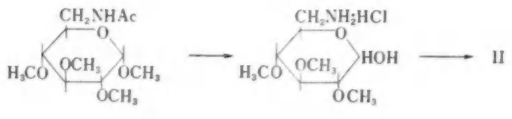
II

the above-mentioned residue from the mother liquor was passed through a column of Amberlite IRC-50 (Na^+ form) to remove *N*-acetylated amino-sugar moieties and developed with dilute hydrochloric acid. The combined residues from the early fractions were subjected to a cellulose powder chromatography to give fractions which showed a single ninhydrin-positive spot and positive Tollens and aniline phthalate reaction. The product was chromatographically identical with the synthetic specimen of 6-amino-6-deoxy-2, 3, 4-tri-*O*-methyl-D-glucose hydrochloride, the synthesis of which is mentioned below. The product could not be caused to crystallize. However, condensation with 2, 4-dinitrofluorobenzene afforded yellow needles of 6-(2, 4-dinitrophenylamino)-6-deoxy-2, 3, 4-tri-*O*-methyl-D-glucose (II).

The synthetic specimen of II has been prepared from 6-amino-6-deoxy-3, 5-benzylidene-1, 2-isopropylidene-D-glucose[5] (III) by the following scheme.



III IV V



VI VII II

1) Presented before the division of Organic Chemistry of the Annual Meeting of the Chemical Society of Japan at Kyoto, April, 1959 and at Tokyo, April, 1960.

2) S. Umezawa, Y. Ito and S. Fukatsu, This Bulletin, 32, 81 (1959).

3) Ref. 2, p. 82.

4) S. Peat and L. F. Wiggins, *J. Chem. Soc.*, **1938**, 1810.

5) B. Helferich and R. Mittag, *Ber.*, **71**, 1588 (1938).

In the course of our synthesis of II, an alternative synthesis of methyl 6-amino-6-deoxy-α-D-glucoside hydrochloride (IV) was performed by Cramer et al.[6] The glucoside prepared by our method has been identified with a sample prepared by the alternative method by the mixed melting point method and infrared absorption spectra.

The mixed melting point determination of the natural and synthetic specimens of II was undepressed and the respective infrared spectra were completely superimposable.

Experimental

Isolation of 3-Acetamido-3-deoxy-2, 4, 6-tri-*O*-methyl-D-glucose (I).—The exhaustively methylated tetra-*N*-acetyl-kanamycin was hydrolyzed with 6 N hydrochloric acid and 1, 3-diamino-4, 6-dihydroxy-5-methoxycyclohexane was separated from the hydrolyzate, details of which were described in a previous paper[1]. The mother liquor was evaporated to dryness. Paperchromatographic studies of the residue (brown syrup) showed ninhydrin-positive spots of R_f 0.54 (violet) 0.41 (violet), 0.31 (orange) 0.23 (violet) and 0.08 (brown) using butanol-ethanol-water (4 : 1 : 5). The residue (9.67 g.) was dissolved in the above-mentioned solvent, chromatographed on a column (3×51 cm.) of cellulose powder and developed with the same solvent. One hundred and fourteen fractions were cut into 10 ml. each, evaporated to dryness, weighed and tested for R_f values. The combined fractions of tube Nos. 27—37 (6.89 g., R_f 0.48, 0.41, 0.36) were again chromatographed in the same manner and the combined fractions of tube Nos. 13–20 were evaporated to yield a crystalline residue (600 mg.). Recrystallization from absolute ethanol afforded needles of m. p. 229~230°C (decomp.), $[\alpha]_D^{15}+107.1°$ (*c* 0.98, methanol).

Found: C, 49.89; H, 7.90; N, 5.49; OCH_3, 35.20; $COCH_3$, 14.70. Calcd. for $C_{13}H_{27}NO_6$: C, 50.18; H, 8.04; N, 5.32; OCH_3, 35.36; $COCH_3$, 16.35%.

The product feebly reduced Fehling's solution and showed a negative ninhydrin reaction. On hydrolysis by refluxing with 6 N hydrochloric acid for 2 hr., the product gave a hydrolyzate which showed a ninhydrin-positive spot of R_f 0.29 (orange). These results indicated that the product was an *N*-acetylated derivative of methylated hexosamine. By refluxing in excess absolute methanol (40 ml.) in the presence of hydrogen chloride (2%), the product (350 mg.) afforded a methyl glucoside (120 mg.) of m. p. 156~157°C, $[\alpha]_D^{15}+120.7°$ (*c* 0.41, chloroform), which had nearly the same m. p. with the methyl 3-acetamido-3-deoxy-2, 4, 6-tri-*O*-methyl-α-D-glucoside reported by Peat and Wiggings[4].

Found: C, 51.87; H, 8.10; N, 5.18; OCH_3, 44.00. Calcd. for $C_{12}H_{25}NO_6$: C, 51.97; H, 8.36; N, 5.05; OCH_3, 44.76%.

The synthetic specimen was therefore prepared from D-glucose by the route of the above authors. The mixed m. p. determination of the natural and synthetic specimen (m. p. 157~158.5°C) was undepressed and the respective infrared spectra were completely superimposable.

Isolation of 6-Amino-6-deoxy-2, 3, 4-tri-*O*-methyl-D-glucose.—The residue (4.89 g.) obtained by evaporation of the mother liquor from 1, 3-diamino-4, 6-dihydroxy-5-methoxycyclohexane was dissolved in water (20 ml.) and passed through a column of Amberlite IRC-50 (Na^+ form, 80 ml.) to remove *N*-acetylated amino-sugar moieties and developed with 0.5 N hydrochloric acid. Thirty-one fractions of eluate were cut into 20 ml. each, evaporated to dryness and tested for R_f values. Fractions of tube Nos. 4–9 showed ninhydrin-positive spots of R_f 0.44~0.46, 0.23~0.24*. The combined residues (4.54 g.) from the fractions were treated with absolute ethanol (30 ml.) to separate off the sodium chloride and the solution was evaporated to dryness to give a syrup (1.60 g.), which was treated with active charcoal in absolute ethanol (20 ml.). To the filtrate was added absolute ether (30 ml.) to precipitate sodium chloride and the filtrate was evaporated. A solution of the resulting syrup (1.39 g.) in methanol (2 ml.) was passed through a column (2×70 cm.) of cellulose powder and developed with *n*-butanol-acetic acid-water (10 : 2 : 5); fifty-seven fractions were cut into 5.0 ml. each. A residue (0.70 g.) obtained from tube Nos. 35–45 showed a single ninhydrin-positive spot of R_f 0.33~0.38 and gave positive Tollens and aniline phthalate reactions. The combined residue (0.60 g.) obtained was mixed with cellulose powder (1.0 g.) in a small quantity of methanol, placed on a column (2×70 cm.) of cellulose powder, washed with *n*-butanol-ligroin-water (19 : 30 : 1) and developed with *n*-butanol-acetic acid-water (10 : 2 : 5); eighty-nine fractions were cut into 5.0 ml. each. Fractions of tube Nos. 43—55 showed a single ninhydrin-positive spot of R_f 0.40 and were chromatographically identical with the synthetic specimen of 6-amino-6-deoxy-2, 3, 4-tri-*O*-methyl-D-glucose hydrochloride.

The combined residues (170 mg.) obtained from the above fractions were dissolved in an aqueous solution (3.0 ml.) of sodium bicarbonate (100 mg.) and to the solutions was added 2, 4-dinitrofluorobenzene (100 mg.) dissolved in absolute ethanol (2.0 ml.); the solution was stirred at room temperature for 1 hr. to give yellow needles. After standing overnight, the needles (180 mg.) were separated and treated with ether to remove a trace of any insoluble part. The ethereal solution was passed through a column of alumina** (10.0 g.) and eluted with ether-petroleum ether and ether in turn. Evaporation of the combined eluates gave a crystalline residue (92 mg.); recrystallization from absolte methanol afforded a pure sample (72 mg.) of 6-(2, 4-dinitrophenylamino)-6-deoxy-2, 3, 4-tri-*O*-methyl-D-glucose (II), m. p. 97~99°C sintered from 92°C), λ_{max}^{EtOH} 261.5 (ε 3833), 348 mμ (ε 8293).

6) F. Cramer, H. Otterbach and H. Springmann, *Chem. Ber.*, **92**, 384 (1959).

* Unless otherwise indicated, the solvent system of *n*-butanol-acetic acid-water (10 : 2 : 5) and Toyo filter paper No. 51 were used.

** Aluminum Oxide, Merck.

Found: C, 46.31; H, 5.20. Calcd. for $C_{15}H_{21}N_3O_9$: C, 46.51; H, 5.46%.

6-Amino-6-deoxy-D-glucose Hydrochloride (IV).—6-Amino-6-deoxy-3,5-benzylidene-1,2-isopropylidene-D-glucose[5] (21.0 g.) was hydrolyzed by refluxing with 75% acetic acid (300 ml.) for 3 hr. and followed by treatment with active charcoal (1.0 g.). The filtrate was evaporated to dryness to give a residue (14.1 g.) which reduced Fehling's solution. To the residue (14.0 g.) which was dried over phosphorus pentoxide in a vacuum desiccator were added silver acetate (10.6 g.), acetic anhydride (11.5 g.) and methanol (141 ml.). The mixture was stirred at room temperature for 3 hr. and refluxed on a water bath for an additional 5 min. The reaction mixture was filtered and washed with hot water; the filtrate was acidified with concentrated hydrochloric acid to Thymol blue to precipitate silver salt. The filtrate was evaporated up to give a crude *N*-acetylated product***, which was dried over phosphorus pentoxide in a vacuum desiccator. The product as converted into a methyl glucoside by refluxing with 300 ml. of methanolic hydrochloride (2%) for 10 hr. The hydrolyzate was neutralized with basic lead carbonate (100 g.), filtered, and the filtrate was evaporated up in vacuo to give a dark syrup, which showed a positive ninhydrin reaction, indicating that de-*N*-acetylation occurred as well as the glucoside formation. The dark product was dissolved in methanol (26 ml.) and the solution was passed through a column of alumina (40 g.), washed with 1 N hydrochloric acid, and developed with methanol; early fractions (170 ml.) were combined and evaporated up to give a brown residue (7.88 g.), An aqueous solution (100 ml.) of the residue was passed through a column of Amberlite IRA-410 (base form, 100 ml.) and the early effluent (77 ml.) was treated with active charcoal (2 g.) and followed by evaporation to dryness to give crude methyl 6-amino-6-deoxy-D-glucoside (3.85 g., overall yield 23%). A solution of the crude product in absolute methanol was acidified with hydrogen chloride and evaporated to dryness. Recrystallization of the resulting solid from absolute methanol-ether afforded colorless crystals (1.5 g.) of methyl 6-amino-6-deoxy-α-D-glucoside hydrochloride, m. p. 200°C. (decomp.).

Methyl 6-Acetamido-6-deoxy-2, 3, 4-tri-*O*-methyl-α-D-glucoside (VI).—A mixture of methyl 6-amino-6-deoxy-α-D-glucoside hydrochloride (3.9 g.), acetic anhydride (15.5 g.) and pyridine (20.7 g.) was stirred at room temperature for 43 hr. The reaction mixture was added to ice water, stirred for 4.5 hr. and then extracted thrice with chloroform (100 ml.). The combined extracts were washed thrice with 35% potassium bisulfate (50 ml.) to remove the pyridine and further washed with a saturated solution (50 ml.) of sodium bicarbonate and water (90 ml.) in turn. The chloroform solution was dried with calcium chloride and evaporated to dryness. To a vigorously stirred solution of the acetylated product (5.90 g.) in methanol (6.0 ml.) was added a solution of dimethyl sulfate (60 ml.) in carbon tetrachloride (24 ml.) and water (4.0 ml.). During this and the subsequent addition of alkali, the temperature of the reaction was kept at about 40°C. A solution of sodium hydroxide (12.5 N, 60 ml.) was added dropwise over a 25 min. period. Again, dimethyl sulfate (20 ml.) was added and 12.5 N sodium hydroxide solution (80 ml.) was added gradually during one-hour period. The reaction mixture was kept at 75°C for 1 hr. and then heated on a boiling water bath for an additional 30 min. The temperature was lowered to about 40°C and the mixture was extracted with two 250-ml. portions of chloroform. After drying with calcium chloride, the combined extract was evaporated to give a crystalline solid (3.80 g. 96.3%). Recrystallization from ethyl acetate gave colorless needles of methyl 6-acetamido-6-deoxy-2,3,4-tri-*O*-methyl-α-D-glucoside, m. p. 121~121.5°C, $[\alpha]_D^{15}$ +250.8° (*c* 1.03, chloroform).

Found: C, 52.13; H, 8.06; N, 5.10; OCH_3, 44.36. Calcd. for $C_{12}H_{23}NO_6$: C, 51.97; H, 8.36; N, 5.05; OCH_3, 44.76%.

6-Amino-6-deoxy-2, 3, 4-tri-*O*-methyl-D-glucose Hydrochloride (VII).—A solution of VI (1.47 g.) in 3 N hydrochoric acid (30 ml.) was refluxed for 6 hr. and treated with active charcoal (100 mg.); the filtrate was evaporated in vacuo. The residue obtained was dissolved in water (30 ml.) and again the solution was evaporated in vacuo. The residue was dried over phosphorus pentoxide in a vacuum desiccator and crystallized from absolute ethanol-absolute ether; colorless needles (1.70 g., 99.6%). Recrystallization from the same solvent gave a pure sample of 6-amino-6-deoxy-2,3,4-tri-*O*-methyl-D-glucose hydrochloride, m. p. 179~180°C (decomp.), $[\alpha]_D^6$ +27.25° → +65.3° (*c* 1.32, water).

Found: C, 42.27; H, 7.56; N, 5.43; OCH_3, 36.37. Calcd. for $C_9H_{20}NO_5Cl$: C, 41.94; H, 7.82; N, 5.43; OCH_3, 36.13%.

6-Deoxy-6-(2, 4-dinitrophenylamino)-2, 3, 4-tri-*O*-methyl-D-glucose.—Condensation of VII with 2,4-dinitrofluorobenzene was accomplished in the same manner as described in the end of the second clause. The crude product (52%) was washed with ether and dissolved in absolute methanol to remove a trace of any insolube part. The residue from the methanol solution was recrystallized from a small quantity of absolute methanol to give an analytically pure sample of m. p. 97~99°C (sintered at about 90°C), $[\alpha]_D^{11}$ +37.7° (*c* 0.61, methanol); λ_{max}^{EtOH} 261.5 (ε 3833), 348 mμ (ε 8393).

Found: C, 46.38; H, 5.24; N, 11.04. Calcd. for $C_{15}H_{21}N_3O_8$: C, 46.51; H, 5.46; N, 10.85%.

*** As direct formation of glucoside from free hexosamine seemed difficult, the glucoside formation was preceded by *N*-acetylation. See T. White, *J. Chem. Soc.*, 1940, 428.

Summary

1) 3-Acetamido-3-deoxy-2, 4, 6-tri-*O*-methyl-D-glucose (I) and *N*-(2, 4-dinitrophenyl) derivative (II) of 6-amino-6-deoxy-2, 3, 4-tri-*O*-methyl-D-glucose have been isolated from the hydrolyzate of exhaustively methylated *N*-acetyl kanamycin.

2) II has been synthesized from 6-amino-6-deoxy-3, 5-benzylidene-1, 2-isopropylidene-D-glucose.

The authors are indebted to Mr. S. Fukatsu for technical assistance in some of the preparations here described and to Mr. S. Nakada for microanalyses.

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Spectrophotometric Determination of Beryllium, Copper and Iron with Sodium-2'', 6''-dichloro-4'-hydroxy-3, 3'-dimethylfuchsone-5, 5'-dicarboxylate

By Yukiteru KATSUBE, Katsuya UESUGI and John H. YOE

(Received May 9, 1960)

Several organic compounds which have the hydroxydimethylfuchsone dicarboxylic acid structure have been used as the reagents for the determination of certain trace metals. Typical of these are eriochrome cyanine R for the colorimetric determination of aluminum[1] and beryllium[2], and chrome azurol S as an indicator for the complexometoric titration of aluminum, copper, iron and zirconium[3-5]. Sodium-2'', 6''-dichloro-4'-hydroxy-3, 3'-dimethylfuchsone-5, 5'-dicarboxylate (pontachrome azure blue B) has been examined spectrophotometrically for the determination of beryllium in an alkaline solution[2], but was not satisfactory because of the overlap of the absorption peak of the reagent with that of its beryllium complex. This paper reports an extensive study of the color reaction between the compound and metallic ions and procedures for its use as a reagent for the spectrophotometric determination of beryllium, copper and iron.

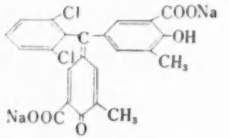

Fig. 1. Sodium-2'', 6''-dichloro-4'-hydroxy-3, 3'-dimethylfuchsone-5, 5'-dicarboxylate.

Experimental

Apparatus and Reagent.—A Shimadzu spectrophotometer model QB-50, with 1.00 cm. glass cells and a Hitachi photoelectric photometer Type-FPW 4 with 1.00 cm. glass cells were used.

Amberlite IRA 410 (50 to 100 mesh) was used in a goose-neck type column (30 cm. in height and 10 mm. in inside diameter).

The reagent solution was prepared by dissolving 0.2 g. of sodium-2'', 6''-dichloro-4'-hydroxy-3, 3'-dimethylfuchsone-5, 5'-dicarboxylate in 100 ml. of 99% ethanol and filtering off the residue.

The standard solution containing 0.1 mg. of beryllium per milliliter was prepared by dissolving beryllium chloride (analytical grade) in distilled water. The standard copper solution containing 0.1 mg. of copper per milliliter was prepared by dissolving pure crystals of $CuSO_4 \cdot 5H_2O$ in distilled water. The standard iron(III) solution was prepared by dissolving crystals of pure $Fe_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$ in dilute sulfuric acid to give a solution containing 0.1 mg. of iron per milliliter. Five grams of 8-hydroxyquinoline was dissolved in 12 ml. of 17 N acetic acid and diluted to 100 ml. with distilled water.

Concentrated ammonium hydroxide (130 ml.) was neutralized with 120 ml. of glacial acetic acid and diluted to 100 ml. with distilled water to give ammonium acetate solution.

Determination of Beryllium.—*Separation of Beryllium.*—Acidify slightly a solution, containing interfering ions such as Al^{3+}, Co^{2+}, Cu^{2+}, $Fe^{2+,3+}$ and Ni^{2+}, with dilute acetic acid, and warm it on a steam bath to 60~70°C. Add the oxine-acetic acid solution in 50% excess, and then add the ammonium acetate solution slowly, until precipitation is complete. Let stand for one hour with frequent stirring, filter off the precipitate and wash with dilute acetic acid. Determine the beryllium in the filtrate.

Procedure of Determination.—Transfer the solution (not more than 1.5 ml.) containing 2 to 20 p.p.m. of beryllium to a 25 ml. volumetric flask, add about 10 ml. of the acetate-acetic acid buffer solution (pH 5.8) and mix well. Then add 1 ml. of the 0.2% reagent solution, shake well, and make up to the

1) F. J. Welcher, "Organic Analytical Reagents", Vol. IV, D. Van Nostrand Co., Inc., New York (1949), p. 355.
2) S. Umemoto, This Bulletin, **29**, 845 (1956).
3) M. R. Lewis and P. P. Goland, *Cancer Research*, **13**, 130 (1953).
4) J. S. Fritz and C. L. Ford, *Anal. Chem.*, **25**, 1640 (1953).
5) M. Theis, *Z. anal. Chem.*, **144**, 275 (1955).
6) K. A. Kraus and G. E. Moore, *J. Am. Chem. Soc.*, **75**, 1460 (1953).

mark with the buffer solution. After 20 min., measure the absorbance at 570 mμ, using a reagent blank solution (or distilled water) as a reference.

Determination of Copper and Iron(III).—*Separation of Copper and Iron.*—Separate copper and iron(III) by the method of Kraus[6], using an anion exchange resin. (Copper and iron do not interfere with each other's determination if the solution is adjusted to pH 7.2 for copper and 3.5 for iron.)

Procedure of Determination.—Transfer 1.00 ml. of the neutralized sample solution containing 10 to 100 p.p.m. of copper (or iron) to a 25 ml. volumetric flask containing about 10 ml. of borax-succinic acid buffer solution (pH 7.2 for copper or 3.5 for iron). Then add 2 ml. of the reagent solution, mix thoroughly, and fill up to the mark with the buffer solution. After 20 min., measure the absorbance at 610 mμ, using a reagent blank solution (or distilled water) as a reference.

For all these measurements, a photoelectric photometer equipped with 570 and 610 mμ filters was used.

Results and Discussion

Color Reactions.—Sodium-2'', 6''-dichloro-4'-hydroxy-3, 3'-dimethylfuchsone-5, 5'-dicarboxylate is a red-brown solid, soluble in water and ethanol. It was stable indefinitely in the solid state and for at least one month when dissolved in ethanol. The effect of pH on the reagent solution is shown in Fig. 2. Its color reaction was tested on a spot plate with 52 ions. Some metallic ions in an acid or a neutral medium reacted with it to give the colors shown in Table I. In an ammoniacal solution, only large amounts of calcium, magnesium and nickel ions gave blue solutions.

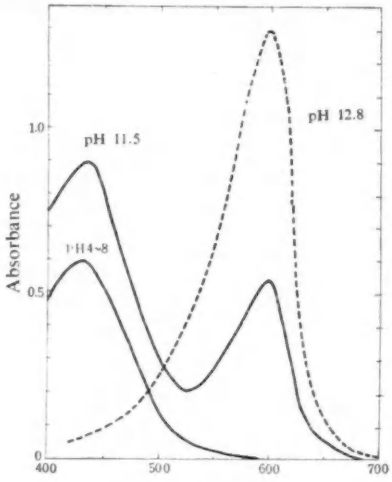

Fig. 2. Effect of pH on the reagent. Reagent: 40 ppm. pH was adjusted by HCl and NaOH solutions.

Seven of the colored complexes were examined spectrophotometrically. The results are summarized in Table II.

Absorption Spectra.—*Beryllium Complex.*—Absorption spectra of the reagent solution and

Table I. Color produced with ions in an acid or a neutral solution

Li^+	*Be^{2+}*													
	Mg^{2+}										*Al^{3+}*			
K^+	Ca^{2+}	*Sc^{3+}*	Ti^{4+}	Cr^{3+}	Mn^{2+}	**Fe^{3+}** **Fe^{2+}**	Co^{2+}	**Ni^{2+}**	**Cu^{2+}**	Zn^{2+}	**Ga^{3+}**	As^{3+}	ScO_2^{2+}	Br^-
Rb^+	Sr^{2+}	**Y^{3+}**	Zr^{4+}			Ru^{3+}	Rh^{3+}	Pd^{4+}	Ag^+		In^{3+}	$Sn^{2+,4+}$	Sb^{3+}	
Cs^+	Ba^{2+}		Hf^{4+}				Ir^{4+}			Hg^+	Tl^{3+}	Pb^{2+}	Bi^{3+}	
				UO_2^{2+}										
*La^{3+}	Ce^{3+} Ce^{4+}	**Pr^{3+}**	**Nd^{3+}**		Eu^{3+}	**Gd^{3+}**		Dy^{3+}		Er^{3+}	Tm^{3+}	Yb^{3+}		

Three ions shown in italic types give green solution.
Ten ions shown in gothic types give blue solution.

Table II. Optimum conditions for analytical use

Ion	Optimum pH	Wavelength at max. absorbance	Buffer soln.	Ion p.p.m. per 0.1 abs. unit
Fe^{3+}	2.8~4.2	610 mμ	B. S.*	0.22
Be^{2+}	5.6~6.2	570	A. A.**	0.02
Al^{3+}	5.6~6.2	600	B. S.	0.06
UO_2^{2+}	5.2	610	—	1.04
Cu^{2+}	6.8~7.8	610	B. S.	0.42
Ca^{2+}	9.0	580	NH_4OH-NH_4Cl	20.0
Mg^{2+}	11.0	570	NH_4OH-NH_4Cl	0.71

* Borax-succinic acid ** Acetate-acetic acid

of its beryllium complex solution are shown in Fig. 3. All solutions were adjusted to pH 5.8, using the acetate-acetic acid buffer solution. The beryllium complex had a maximum absorption at 570 mμ. However, the reagent appreciably absorbed light at 570 mμ when its concentration was more than 50 p.p.m.

Copper and Iron(III) Complex. — The copper complex in a solution of pH 7.2 had a maximum absorption at 610 mμ; the reagent did not appreciably absorb light at this wavelength when its concentration was less than 100 p.p.m. The iron(III) complex in a solution of pH 3.5 had also a maximum absorption at 610 mμ.

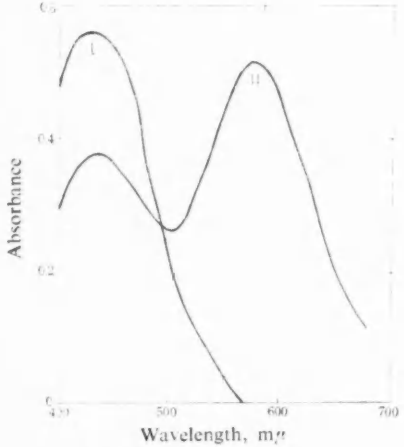

Fig. 3. Absorption spectra.
I: Reagent, 30 p.p.m.
II: Reagent (30 p.p.m.) – Be(0.1 p.p.m.)
pH: 5.8

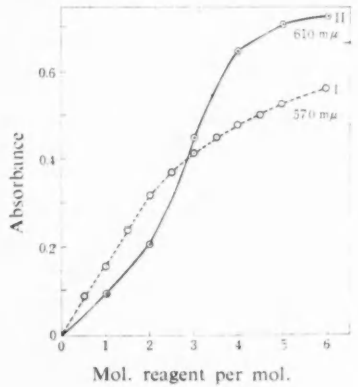

Fig. 4. Application of the mole ratio method.
I: Beryllium complex (pH 5.8)
II: Copper complex (pH 7.2)

7) J. H. Yoe and A. I. Jones, *Ind. Eng. Chem., Anal. Ed.*, **16**, 111 (1944).

Mole Ratio Studies. — *Beryllium Complex.* — Application of the mole ratio method[7] showed no sharp break or leveling-off to a constant absorbance for ratios up to as high as one mole of beryllium to six moles of reagent. The results are shown in Fig. 4.

Obviously the colored complex is appreciably dissociated and hence a large excess of the reagent is required to cause the reaction to proceed completion. By the application of the continuous variation method[8], the ratio of beryllium to the reagent was shown to be 1 to 2 (see Fig. 5).

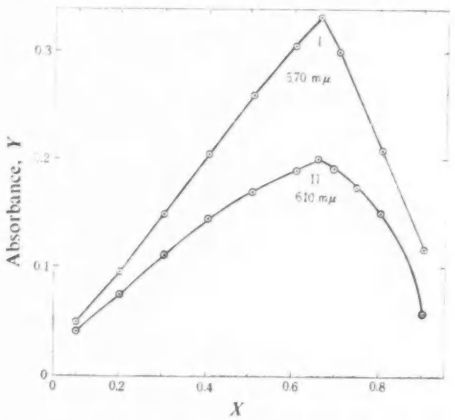

Fig. 5. Application of the method of continuous variation.
I: Be-complex (pH 5.8), II: Cu-complex (pH 7.2).

The best analytical results were obtained when the concentration of unreacted reagent was between 50 and 80 p.p.m.

Copper and Iron(III) Complexes.—Mole ratio studies for copper complex solution (pH 7.2) gave results similar to those for beryllium; the copper complex was appreciably dissociated and the ratio of copper to the reagent was 1 to 2 (see Figs. 4 and 5). The iron complex was also studied in a solution of pH 3.5. The ratio of iron to the reagent was 1 to 3.

Effect of pH. — Borax-succinic acid buffer and acetate-acetic acid buffer were satisfactory for the determination of beryllium, copper and iron. For an accurate measurement it was necessary to hold the pH fairly constant. The effect of pH on the color intensities of the metal complexes is shown in Fig. 6. The optimum pH range for the determination is listed in Table II.

Effect of Temperature.—There was no variation in the absorbance of the color systems

8) W. C. Vosburgh and G. R. Cooper, *J. Am. Chem. Soc.*, **63**, 437 (1941).

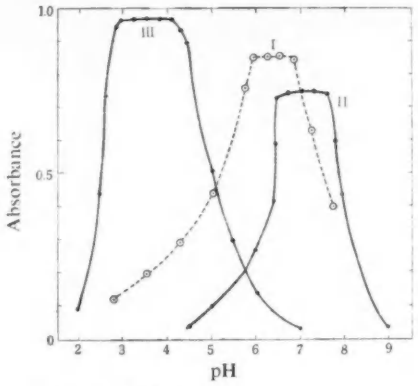

Fig. 6. Effect of pH.
I: Be^{+2}, 0.17 p.p.m., II: Cu^{+2}, 3.0 p.p.m., III: Fe^{+3}, 2.0 p.p.m.

over a temperature range of 15 to 30°C Hence, normal temperature changes in the laboratory introduce no error.

Rate of Color Development. — At room temperature the color intensities increased during the first 20 min. then remained constant for 40 to 50 min.

Interfering Ions.—Color reactions of 52 ions are listed in Table I. The limiting concentrations of seven ions in the determination of beryllium are given in Table III. The concentration of an ion that causes a diviation of 0.01 unit in the absorbance of a solution containing 0.1 p.p.m. of beryllium was taken to be the limiting concentration.

TABLE III. LIMITING CONCENTRATIONS OF INTERFERING IONS FOR DETERMINATION OF BERYLLIUM

Ion	Added as	Limiting concentration p.p.m.
Al^{+3}	$K_2SO_4Al_2(SO_4)_3$	0.09
Co^{+2}	$Co(NO_3)_2$	20.0
Cr^{+3}	$Cr_2(SO_4)_3$	3.0
Cu^{+2}	$CuSO_4$	0.22
Fe^{+3}	$K_2SO_4Fe_2(SO_4)_3$	0.27
Ni^{+2}	$Ni(NO_3)_2$	16.4
UO_2^{+2}	$UO_2(NO_3)_2$	1.9

Several methods were tried to eliminate the interfering ions for the determination of beryllium. The 8-hydroxyquinoline method[9] effected a good separation of beryllium. Interfering ions for the determination of copper and iron, such as Al^{+3}, Be^{+2}, Co^{+2} and Cr^{+3}, were eliminated by the method of Kraus[6].

9) E. B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd Ed., Interscience Publishers, Inc., New York (1959), p. 306.

Beer's Law.—As a large excess of the reagent required for the determination of beryllium, was copper and iron, the calibration curves of water blank did not pass through the origin because of the absorption of the reagent solution at 570 or 610 mμ. The use of these curves provided satisfactory results whenever the same concentration of the reagent was used for

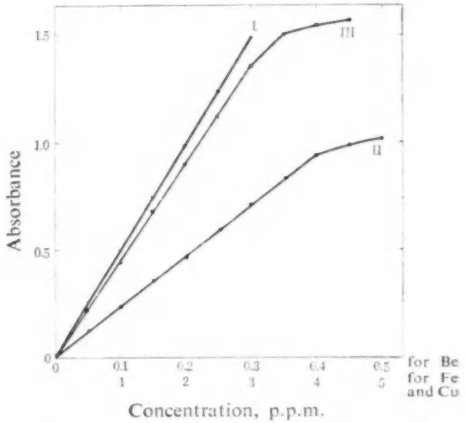

Fig. 7. Calibration curves for the determination.
I: Be^{+2}, pH 5.8, II: Cu^{+2}, pH 7.2, III: Fe^{+3}, pH 3.5, reference: reagent blank.

TABLE IV. DETERMINATION OF BERYLLIUM

	Solution analized		Found Be* p.p.m.	Error %
	Ion	Added p.p.m.		
1)	Al^{+3}	0.16		
	Fe^{+2}	0.16		
	Co^{+2}	0.16		
	Ni^{+2}	10.00		
	Cu^{+2}	20.00		
	Zn^{+2}	20.00		
	Be^{+2}	0.16	0.16	0.0
2)	Al^{+3}	8.00		
	Fe^{+3}	10.00		
	Co^{+2}	10.00		
	Ni^{+2}	20.00		
	Cu^{+2}	20.00		
	Ti^{+4}	20.00		
	Be^{+2}	0.16	0.15	−6.3
3)	Al^{+3}	10.00		
	Cr^{+3}	10.00		
	Cu^{+2}	10.00		
	Fe^{+3}	20.00		
	Ca^{+2}	20.00		
	Mg^{+2}	20.00		
	Ni^{+2}	10.00		
	Be^{+2}	0.08	0.08	0.0

* These values are the averages of six repeated determinations.

standards and unknowns. However, color intensities measured with the reagent solution as a blank obeyed Beer's law better than those with a water blank; Beer's law was obeyed up to about 0.3 p.p.m. of beryllium, about 4.0 p.p.m. of copper and about 3.0 p.p.m. of iron (see Fig. 7). In addition, the absorbances were sufficiently reproducible to permit beryllium to be determined up to 0.4 p.p.m., but for the best precision the concentration range should be 0.05 to 0.3 p.p.m.

TABLE V. DETERMINATION OF COPPER AND IRON

	Solution analyzed		Found*		Error
	Ion	Added p.p.m.	Cu p.p.m.	Fe	%
1)	Cu^{2+}	2.00	2.01		+0.5
	Fe^{3+}	2.00		1.96	−2.0
2)	Al^{3+}	20.00			
	Ca^{2+}	20.00			
	Be^{2+}	2.00			
	Cu^{2+}	1.00	1.01		+1.0
	Fe^{3+}	1.00		0.97	−3.0
3)	Al^{3+}	200.00			
	Ca^{2+}	200.00			
	Mg^{2+}	200.00			
	Cu^{2+}	2.00	1.88		−6.0
	Fe^{3+}	2.00		1.86	−7.0

* These values are the averages of three repeated determinations.

Determination of Beryllium in Solutions Containing Various Ions. — Beryllium has been determined in three solutions containing various amounts of certain foreign ions, after separation of the latter by oxine precipitation. The results are listed in Table IV.

Determination of Copper and Iron in Solutions Containing Various Ions.—Copper and iron(III) have been determined in three solutions, after separation of the foreign ions by the exchange resin. The results are given in Table V.

Summary

Procedures have been developed for the spectrophotometric determination of trace amounts of beryllium, copper and iron(III) with sodium-2'', 6''-dichloro-4'-hydroxy-3, 3'-dimethylfuchsone-5,5'-dicarboxylate. Certain ions that interfere with the beryllium determination are removed by an oxine precipitation. Ions that interfere with the analysis of copper and iron(III) are removed with an anion exchange resin column.

Accuracy and precision are good. Beer's law is obeyed up to about 0.3 p.p.m. of beryllium, about 4 p.p.m. of copper and about 3 p.p.m. of iron.

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Electronic Spectra of Substituted Aromatic Hydrocarbons. I. Phenol and Aniline

BY Hiroaki BABA

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Recent advances in both theoretical[1-4] and experimental[5,6] studies have made it possible to understand fully the origin of the electronic spectra of aromatic hydrocarbons. On the other hand, it appears that no satisfactory interpretations have been given to the spectra of substitution products of the aromatics other than benzene. The present series of papers are concerned with systematic analyses of the electronic spectra of substituted aromatic hydrocarbons, especially hydroxyl and amino derivatives.

As to the spectra of monosubstituted benzenes, a number of theoretical investigations have been carried out[7-13]. There remain, however, unsettled problems even concerning

1) J. R. Platt, *J. Chem. Phys.*, **17**, 484 (1949).
2) J. A. Pople, *Proc. Phys. Soc.*, **A68**, 81 (1955).
3) R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).
4) N. Mataga, K. Nishimoto and S. Mataga, This Bulletin, **32**, 395 (1959).
5) H. B. Klevens and J. R. Platt, *J. Chem. Phys.*, **17**, 470 (1949).
6) D. S. McClure, ibid., **22**, 1668 (1954); J. W. Sidman, ibid., **25**, 115 (1956).
7) A. L. Sklar, ibid., **7**, 984 (1939).
8) K. F. Herzfeld, *Chem. Revs.*, **41**, 233 (1947).
9) F. A. Matsen, *J. Am. Chem. Soc.*, **72**, 5243 (1950).
10) S. Nagakura and H. Baba, ibid., **74**, 5693 (1952).
11) L. Goodman and H. Shull, *J. Chem. Phys.*, **27**, 1388 (1957).
12) K. Nishimoto and R. Fujishiro, This Bulletin, **31**, 1036 (1958).
13) Y. I'Haya, *J. Am. Chem. Soc.*, **81**, 6120, 6127 (1959).

the qualitative assignment of the observed absorption bands. In this paper, a molecular orbital (MO) calculation has been made of the π-electronic spectra of phenol and aniline. Herein a semiempirical method of calculation is developed, which will be applied also to naphthalene derivatives in the next paper.

Method of Calculation

The so-called simple LCAO MO theory originally proposed by Hückel is inadequate for dealing with molecules in their excited states. The more rigorous theoretical method, which is based on the correct many-electron Hamiltonian, has been developed to account for the electronic spectra of unsaturated compounds. Although the latter method has been simplified by Pariser and Parr[14] and Pople[2], it seems troublesome to apply it directly to such complex molecules as monosubstituted naphthalenes.

In this calculation an eclectic method is adopted; namely, the simplicity of the Hückel theory is retained, and at the same time it is somewhat modified by reference to the rigorous theoretical method so as to allow for electronic interaction. Thus, MO's are determined by the simple LCAO procedure; configurational wave functions are built up as antisymmetrized products of these MO's, configuration interaction being taken into account.

In the simple LCAO procedure, the energy of an MO is expressed in termes of the resonance integral β [$\equiv\beta_{CC}$]. In the present calculation, the evaluation of this integral is made, after the scheme of Goodman and Shull[11], in the following way.

According to the simple LCAO MO theory, the energy required for exciting an electron from an occupied MO ϕ_i to an unoccupied MO ϕ_k is given by

$$\Delta E = e_k - e_i = (m_k - m_i)\beta \qquad (1)$$

Here, e_i and e_k are the energies of the MO's ϕ_i and ϕ_k, respectively; $e_i=\alpha+m_i\beta$ and $e_k=\alpha+m_k\beta$, where α [$\equiv\alpha_C$] is the Coulomb integral of a carbon atom.

In the rigorous theory, configurational wave functions are obtained as antisymmetrized products of molecular spin-orbitals. Such wave functions for the lowest energy configuration and for the singlet configuration resulting from the excitation $\phi_i \rightarrow \phi_k$ are denoted by V_0 and V_{ik}, respectively. The energies associated with these wave functions are

$$E(V_0) = \int V_0^* \mathbf{H} V_0 \, d\tau, \quad \text{etc.}$$

where **H** is the complete many-electron Hamiltonian. Deriving an expression for the excitation energy $\Delta E = E(V_{ik}) - E(V_0)$ by the self-consistent field method, Mulliken pointed out that the energy quantity which is acceptable as the energy of the excited MO ϕ_k is dependent not only upon the MO ϕ_k, but also upon the MO ϕ_i from which the excitation occurs[15]. On the contrary, the orbital energy e_k in Eq. 1 does not depend on ϕ_i.

In view of this situation, let the resonance integral be regarded as a quantity depending upon both i and k, and be designated as $\beta_{i\rightarrow k}$ instead of β. Then, the following relation may be assumed to hold[16]

$$(m_k - m_i)\beta_{i\rightarrow k} = E(V_{ik}) - E(V_0) \qquad (2)$$

If the purely theoretical quantity, $E(V_{ik}) - E(V_0)$, is replaced by an appropriate experimental one, $\beta_{i\rightarrow k}$ will immediately be determined, for the values of m_i and m_k can be obtained from the simple MO procedure.

In this study only the singlet transitions will be treated.

Results of Calculation

Molecular Orbitals. — The MO's have been determined by the simple LCAO MO theory with neglect of overlap integrals.

In the parent hydrocarbon, benzene, the following four MO's are responsible for the lower electronic transitions:

$$\phi_2^0 = (1/2)(\chi_2 + {}_3\chi - \chi_5 - \chi_6) \qquad (3a)$$

$$\phi_3^0 = (1/\sqrt{12})(2\chi_1 + \chi_2 - \chi_3 - 2\chi_4 - \chi_5 + \chi_6) \qquad (3b)$$

$$\phi_4^0 = (1/\sqrt{12})(2\chi_1 - \chi_2 - \chi_3 + 2\chi_4 - \chi_5 - \chi_6) \qquad (3c)$$

$$\phi_5^0 = (1/2)(-\chi_2 + \chi_3 - \chi_5 + \chi_6) \qquad (3d)$$

where χ_p is the pth carbon $2p\pi$ atomic orbital; the superscript zeros refer to the parent hydrocarbon; ϕ_2^0, ϕ_3^0 and ϕ_4^0, ϕ_5^0 are degenerate pairs of MO's, viz., $e_2^0 = e_3^0 = \alpha + \beta$, $e_4^0 = e_5^0 = \alpha - \beta$.

In the calculation of the MO's of a monosubstituted benzene, the Coulomb integral α_X of the substituent X is taken as

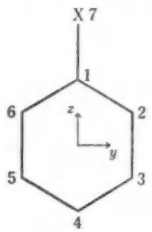

Fig. 1.

14) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466, 767 (1953).

15) R. S. Mulliken, *J. chim. phys.*, **46**, 497 (1949); R. G. Parr and R. S. Mulliken, *J. Chem. Phys.*, **18**, 1338 (1950).

16) A more detailed discussion on this point is given in H. Baba and S. Suzuki, ibid., **32**, 1706 (1960).

$$\alpha_X = \alpha + \delta_X \beta$$

The MO's and their energies are calculated for various values of the parameter δ_X. Let the MO of the monosubstituted benzene corresponding to ϕ_i^0 of the parent hydrocarbon be designated as ϕ_i, and suppose that the substituent X is attached to the carbon atom 1, as shown in Fig. 1. Then, the MO's ϕ_2 and ϕ_5 of symmetry type a_2 are identical with ϕ_2^0 and ϕ_5^0, respectively[17]; the MO's ϕ_3 and ϕ_4 are of symmetry type b_1. The variation of the MO energies with the magnitude of δ_X was reported by Matsen[9].

Configuration Energies.—Owing to the high symmetry (D_{6h}) of benzene, V_{24}^0, V_{35}^0 and V_{25}^0, V_{34}^0 are degenerate pairs of configurations, and the interaction of the configurations of each pair is automatically introduced to give excited states, the characteristics of which are shown

TABLE I. EXCITED STATES OF BENZENE

Symmetry D_{6h}	Symmetry C_{2v}*	Wave function	Observed excitation energy**, eV.
B_{2u}	B_2^-	$\frac{1}{\sqrt{2}}(V_{24}^0 - V_{35}^0)$	4.88
B_{1u}	A_1^+	$\frac{1}{\sqrt{2}}(V_{25}^0 + V_{34}^0)$	6.14
E_{1u}	B_2^+	$\frac{1}{\sqrt{2}}(V_{24}^0 + V_{35}^0)$	6.74
	A_1^-	$\frac{1}{\sqrt{2}}(V_{25}^0 - V_{34}^0)$	

* In this column are given symmetry types for the subgroup C_{2v} of D_{6h}. The plus or minus sign refers to the manner in which two configurations combine with each other.

** Taken from Ref. 18.

in Table I. Referring to this table, one obtains

$$E(V_{24}^0) = E(V_{35}^0) = \frac{1}{2}\{W^0(B_{2u}) + W^0(E_{1u})\}$$
$$= E(V_0^0) + 5.81 \text{ eV}.$$
$$E(V_{25}^0) = E(V_{34}^0) = \frac{1}{2}\{W^0(B_{1u}) + W^0(E_{1u})\}$$
$$= E(V_0^0) + 6.44 \text{ eV}.$$

in which $W^0(B_{2u})$, for instance, represents the energy of the B_{2u} state of the parent hydrocarbon, benzene. Since $m_2^0 = m_3^0 = 1$, $m_1^0 = m_5^0 = -1$, it follows from Eq. 2 that

$$\beta_{2\to4}^0 = \beta_{3\to5}^0 = -2.905 \text{ eV}. = \beta^0(B_2) \quad (4a)$$
$$\beta_{2\to5}^0 = \beta_{3\to4}^0 = -3.22 \text{ eV}. = \beta^0(A_1) \quad (4b)$$

In the monosubstituted benzene, the energies of the B_2 configurations, V_{24} and V_{35}, are no longer equal to each other; the same is the case with the energies of the A_1 configurations, V_{25} and V_{34}. In evaluating the energies of these configurations, the assumption is made that

$$\beta_{2\to4} = \beta_{3\to5} = \beta^0(B_2) \quad (5a)$$
$$\beta_{2\to5} = \beta_{3\to4} = \beta^0(A_1) \quad (5b)$$

Then the energies $E(V_{ik})$'s for the configurations V_{ik}'s are readily derived on the basis of Eq. 2, since m_i and m_k can be obtained from the simple MO calculation.

Configuration Interaction.—The matrix element of the total Hamiltonian **H** between V_{ik} and V_{jl} is, in general, given by

$$\{V_{ik} \mid V_{jl}\} = \int V_{ik}^* \mathbf{H} V_{jl}\, dv$$
$$= 2[ki \mid jl] - [kl \mid ji] \quad (i \neq j,\ k \neq l) \quad (6)$$

with

$$[ij \mid kl] = \int \phi_i^*(1)\phi_k^*(2)(e^2/r_{12})\phi_j(1)\phi_l(2)dv \quad (7)$$

The orthonormal MO's determined by the simple MO theory are used for the calculation of the above matrix element. On the assumption of zero differential overlap, the integral $[ij \mid kl]$ may be expressed in terms of integrals over atomic orbitals of the form

$$(pp \mid qq) = \int \chi_p^*(1)\chi_q^*(2)(e^2/r_{12})\chi_p(1)\chi_q(2)dv \quad (8)$$

The integrals of this type were evaluated by Pariser and Parr's method[14]. Necessary values of the valence-state ionization potentials and electron affinities for carbon, oxygen and nitrogen atoms were taken from the table of Pritchard and Skinner[19]. The values of the integrals $(11 \mid 11)_{CC}$ and $(11 \mid 22)_{CC}$ were slightly modified in the following manner.

To the approximation adopted in the present calculation, one obtains

$$\{V_{24}^0 \mid V_{25}^0\} = (1/12)\{(11 \mid 11)_{CC} + 3(11 \mid 22)_{CC} - (11 \mid 33)_{CC} - 3(11 \mid 44)_{CC}\}$$
$$= (1/2)\{W^0(E_{1u}) - W^0(B_{2u})\} \quad (9a)$$
$$\{V_{25}^0 \mid V_{34}^0\} = (1/12)\{(11 \mid 11)_{CC} - 9(11 \mid 22)_{CC} + 11(11 \mid 33)_{CC} - 3(11 \mid 44)_{CC}\}$$
$$= (1/2)\{W^0(B_{1u}) - W^0(E_{1u})\} \quad (9b)$$

17) Monosubstituted benzenes belong to symmetry group C_{2v}. The group-theoretical notation used in this paper is the same as that of G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", D. Van Nostrand Company, Inc., New York (1945), p. 106. The y and z axes are chosen as in Fig. 1 and the x axis is perpendicular to the molecular plane.

18) H. B. Klevens and J. R. Platt, "Technical Report, Laboratory of Molecular Structure and Spectra, Univ. of Chicago", Part One (1953-1954), p. 145.

19) H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, 55, 745 (1955).

in which the superscript zeros refer, as before, to benzene. Pariser and Parr's method gives $(11 \mid 33)_{cc}=5.470$ eV. and $(11 \mid 44)_{cc}=4.894$ eV. Inserting these values into Eqs. 9a and 9b and using the experimental values, quoted in Table I, for $W^0(B_{2u})$, etc., one may determine those values of $(11 \mid 11)_{cc}$ and $(11 \mid 22)_{cc}$ which simultaneously satisfy Eqs. 9a and 9b. The result is

$$\left.\begin{aligned}(11 \mid 11)_{cc}&=11.212\text{ eV.}\quad(10.84\text{ eV.})\\(11 \mid 22)_{cc}&=\ 6.700\text{ eV.}\quad(7.392\text{ eV.})\end{aligned}\right\} \tag{10}$$

the values obtained by the method of Pariser and Parr being given in parentheses.

The matrix elements $\{V_{24} \mid V_{35}\}$ and $\{V_{25} \mid V_{34}\}$ for the monosubstituted benzene are calculated to be

$$\begin{aligned}&\{V_{24} \mid V_{35}\}\\&=(1/2)(-g_{22}+g_{23})\{(11 \mid 11)_{cc}-(11 \mid 33)_{cc}\}\\&+(3/2)(g_{32}-g_{23})\{(11 \mid 22)_{cc}-(11 \mid 44)_{cc}\}\end{aligned} \tag{11a}$$

$$\begin{aligned}&\{V_{25} \mid V_{34}\}\\&=(-g_{22}+g_{33})\{(1/2)(11 \mid 11)_{cc}-(11 \mid 22)_{cc}\\&+(3/2)(11 \mid 33)_{cc}-(11 \mid 44)_{cc}\}\\&+(1/2)(g_{32}-g_{23})\{(11 \mid 22)_{cc}-(11 \mid 44)_{ec}\}\\&-(g_{11}-g_{14})\{(11 \mid 22)_{cc}-(11 \mid 33)_{cc}\}\\&-g_{77}\{(22 \mid 77)_{cX}-(33 \mid 77)_{cX}\}\end{aligned} \tag{11b}$$

Here $g_{pq}=c_{3p}c_{4q}$, in which c_{ip} is the coefficient of the atomic orbital χ_p in MO ϕ_i. The matrix elements have been computed for various values of δ_X, the results being shown in Fig. 2. Actually, the curve for $\{V_{25} \mid V_{34}\}$ was obtained by assuming X to be NH_2. It should be noted in this connection that, while $\{V_{24} \mid V_{35}\}$ does not contain any terms associated with the substituent X, $\{V_{25} \mid V_{34}\}$ does contain such terms (see Eq. 11b). Accordingly, a deviation from the above-mentioned curve may occur when X is taken to be OH instead of NH_2. An examination on this point, however, revealed that the deviation is so small as to be virtually negligible. Consequently the curve in question can be applied to the case of the hydroxyl substituent as well as to the amino substituent.

State Energies.—The interaction between the two B_2 configurations, V_{24} and V_{35}, gives two B_2 states, B_2^+ and B_2^-. Similarly A_1^+ and A_1^- states arise from the interaction of V_{25} and V_{34}. The dependencies of the energies of these states upon δ_X are shown in Fig. 3, together with the observed excitation energies[18,20] for phenol and aniline.

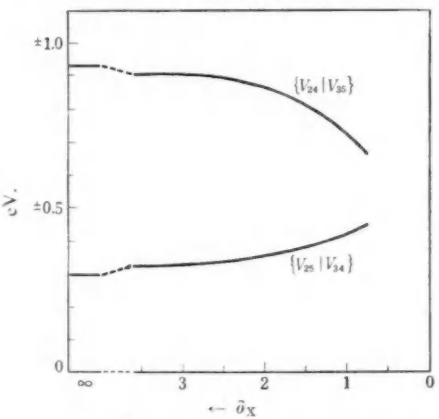

Fig. 2. Relation of the configuration interaction integrals to δ_X. The plus and minus signs on the scale numbers of the ordinate correspond to $\{V_{24} \mid V_{35}\}$ and $\{V_{25} \mid V_{34}\}$, respectively.

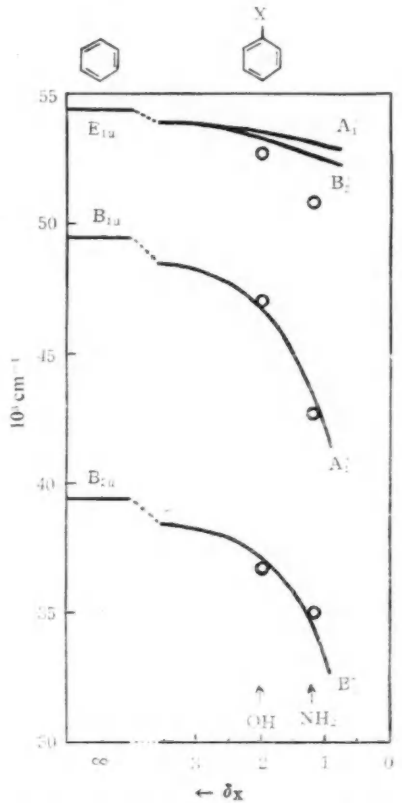

Fig. 3. Relation of the energies of the excited states to δ_X. The observed energies are represented by circles.

20) American Petroleum Institute Research Project 44, Ultraviolet Spectral Data, Serial No. 171.

Oscillator Strengths.—The oscillator strengths, f, have been calculated by the use of the well-known relation[21]

$$f = 1.085 \times 10^{11} \nu \mathbf{Q}^2 \qquad (12)$$

where ν is wave number in cm^{-1} and $\mathbf{Q}$ is transition moment in cm. The results are graphed in Fig. 4. The directions of the transition moments are known from the symmetry types of the excited states concerned. Thus the moments of the transitions to the $B_2^{\pm}$ states are perpendicular to the C_1–X axis, while those of the transitions to the $A_1^{\pm}$ states lie along the direction of the C_1–X axis.

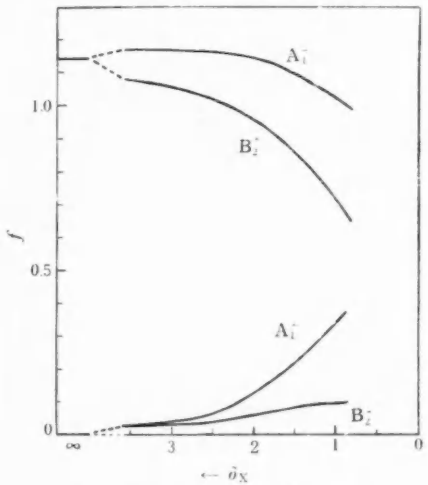

Fig. 4. Relation of f values to δ_X.

Changes of Electron Density Accompanying Electronic Transitions.—The changes of the π-electron density at the substituent X, Δq_X, accompanying the electronic transitions have been calculated as functions of δ_X. The results are shown in Fig. 5. The calculation of the electron density is based on the definition of Pariser[3].

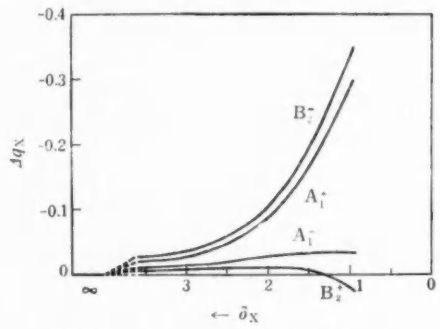

Fig. 5. Relation of Δq_X values to δ_X.

Summary of Calculation.—In the preceding sections several theoretical quantities, e.g., configuration interaction integrals and energies of excited states, have been given as functions of the parameter δ_X to see the general trend of the substitution effects. However, in order to find the values of these quantities for a particular molecule, one must assign a suitable value to δ_X. In this calculation the values of δ_X for phenol and aniline have been determined in such a way that the calculated excitation energies might be in best agreement with the observed. This led to the following parameter values (cf. Fig. 3):

$$\text{phenol,} \quad \delta_O = 2.0 \qquad (13a)$$

$$\text{aniline,} \quad \delta_N = 1.2 \qquad (13b)$$

Other theoretical quantities than the excitation energies are also derived by using these parameter values. The calculated results thus obtained for phenol and aniline are summarized in Tables II and III, together with available experimental data.

Discussion

It is seen from Table III that the degrees of configuration mixing in the wave functions of the excited states are considerably changed upon substitution. As was pointed out by Goodman and Shull[11], this fact is of basic importance in discussing the effect of substitution on the excitation energies and intensities.

In making the assignment of the electronic transitions of the substituted benzenes, particularly of aniline, a problem is raised concerning the nature of the excited state for the transition corresponding to the $A_{1g} \rightarrow B_{1u}$ transition of benzene. Murrell[22] regarded the absorption band at 42700 cm^{-1} in aniline as due to a transition to an electron transfer state characteristic of this molecule. According to the present calculation, the above band is attributed to the transition to the A_1^+ state of aniline which corresponds to the B_{1u} state of benzene. As is seen from the data on Δq_N of Table III, this transition is accompanied by an electron transfer, but its amount is much smaller than that in the electron transfer transition of Murrell. Moreover, there occurs an electron transfer also in the transition to the B_2^- state, the amount of which is comparable to that in the case of the transition to the A_1^+ state. Inspection of the calculated values of Δq_X will show that there is no substantial difference between the natures of

21) R. S. Mulliken and C. A. Rieke, *Repts. Progr. Phys.*, **8**, 231 (1941).

22) J. N. Murrell, *Proc. Phys. Soc.*, **A68**, 969 (1955).

TABLE II. ORBITAL ENERGIES AND ORBITALS FOR PHENOL AND ANILINE

	i	Orbital energy $(e_i-\alpha)/\beta$	Orbital ϕ_i
Phenol	3	0.755	$0.477\chi_1-0.372(\chi_2+\chi_6)-0.197(\chi_3+\chi_5)-0.520\chi_4-0.384\chi_7$
	4	−1.108	$0.569\chi_1-0.224(\chi_2+\chi_6)-0.321(\chi_3+\chi_5)+0.580\chi_4-0.183\chi_7$
Aniline	3	0.575	$0.356\chi_1-0.387(\chi_2+\chi_6)-0.133(\chi_3+\chi_5)-0.463\chi_4-0.569\chi_7$
	4	−1.143	$0.559\chi_1-0.200(\chi_2+\chi_6)-0.330(\chi_3-\chi_5)+0.577\chi_4-0.238\chi_7$

TABLE III. EXCITED STATES OF PHENOL AND ANILINE

	Symmetry	Wave function	Excitation energy, cm^{-1}		f		Δq_X
			calcd.	obs.*	calcd.	obs.**	calcd.
Phenol	B_2^-	$0.495V_{24}-0.869V_{35}$	37200	36700	0.059(0.018)	0.0213	−0.103
	A_1^+	$0.487V_{25}-0.873V_{34}$	46800	47000	0.125(0.037)	0.103	−0.087
	B_2^+	$0.869V_{24}+0.495V_{35}$	53400	52700	0.956(0.29)		−0.011
	A_1^-	$0.873V_{25}-0.487V_{34}$	53600		1.142(0.34)		−0.027
Aniline	B_2^-	$0.366V_{24}-0.931V_{35}$	34500	35000	0.091(0.027)	0.026	−0.273
	A_1^+	$0.356V_{25}-0.935V_{34}$	43400	42700	0.289(0.087)	0.17	−0.233
	B_2^+	$0.931V_{24}-0.366V_{35}$	52700	50800	0.773(0.23)		+0.006
	A_1^-	$0.935V_{25}-0.356V_{34}$	53200		1.051(0.32)		−0.034

* Taken from Refs. 18 and 20.
** Values for phenol are obtained from the unpublished data of the present author, and those for aniline from the data of Ref. 20.

the 42700 cm^{-1} band of aniline and of the 47000 cm^{-1} band of phenol. Thus, as to the origin of the aniline band, the present interpretation is somewhat different from Murrell's. A further experimental examination is desirable for reaching a final conclusion.

In both phenol and aniline, the calculated energy levels of the B_2^+ and A_1^- states are situated close to each other. This suggests that the 52700 cm^{-1} band of phenol, or the 50800 cm^{-1} band of aniline, consists of two absorptions corresponding to the excitations to the B_2^+ and A_1^- states.

The calculated values of the oscillator strengths may account for the general feature of the effect of the substitution on the band intensities, but their absolute values are too high. A correction factor of 0.30 was introduced, which is the ratio of f_{obs} to f_{calcd} for the $A_{1g}\rightarrow E_{1u}$ transition in benzene; the corrected values are given in parentheses in Table III.

In making a comparison of the calculated and observed f values, one should keep the following point in mind. Both the $A_{1g}\rightarrow B_{2u}(B_2^-)$ and $A_{1g}\rightarrow B_{1u}(A_1^+)$ transitions in benzene are theoretically forbidden, i.e., $f_{calcd}=0$; whereas f_{obs} values for these transitions were found to be 0.0014 and 0.10, respectively[18]. This discrepancy was shown to be due to the distortion of the ring by unsymmetrical vibrations[23]. A part of the f_{obs} values for the corresponding transitions of the substituted benzenes may come from such a ring distortion effect[24]. This is not taken into consideration in deriving the f_{calcd} values. If allowance is made for the contribution from the ring distortion effect, the f_{obs} values for phenol and aniline are known to be in fairly good agreement with the corrected values of f_{calcd}.

The calculation of Δq_X provides useful information about the charge distributions in the excited states. It is seen in Table III that all the Δq_X values are negative except for that associated with the B_2^+ state of aniline, and that the magnitudes of Δq_X for the B_2^- and A_1^+ states are noticeably greater than those for the B_2^+ and A_1^- states. In the ground state of the substituted benzenes under consideration, the substituent has a formal positive charge on account of the migration of the non-bonding pair of electrons into the benzene ring[25]. It will be expected from the calculation that the transitions to the B_2^- and A_1^+ states are accompanied by an appreciable increase of the said positive charge. This expectation is consistent with the observation that the absorption bands corresponding to the transitions to the B_2^- and A_1^+ states are distinctly shifted to the longer wavelengths by the formation of a hydrogen bond between phenol or aniline and

23) A. L. Sklar, *J. Chem. Phys.*, **5**, 669 (1937); M. Goeppert-Mayer and A. L. Sklar, ibid., **6**, 645 (1938); H. Sponer, G. Nordheim, A. L. Sklar and E. Teller, ibid., **7**, 207 (1939).
24) A. L. Sklar, ibid., **10**, 135 (1942).
25) The charge distribution in the ground state of aniline will be shown in the next paper.

a proton-accepting substance, e.g., dioxane[26].

In consideration of the electronegativities of oxygen and nitrogen, the magnitudes of the Coulomb integral parameters δ_O and δ_N, given in Eqs. 13a and 13b, appear to be reasonable. However in the present treatment no allowance has been made for the inductive effect of the substituent group on the ring carbon atoms, which is to be taken into account in a more precise calculation; further, the resonance integral β_{CX} has been assumed to be equal to β_{CC}. Accordingly, the values of δ_O and δ_N should be regarded as effective ones. At any rate, in view of its practical nature, the present method of calculation is expected to be useful for dealing with the spectra of substitution products of complex organic compounds.

26) H. Baba and S. Suzuki, to be published in *J. Chem. Phys.*

Summary

The electronic spectra of monosubstituted benzenes are examined from the viewpoint of semi-empirical MO theory. To allow for electronic interaction, the simple LCAO method is refined in the light of purely theoretical procedure, configuration interaction being included. The refined method is particularly convenient for dealing with the spectra of substituted organic compounds.

The origins of the absorption bands for phenol and aniline are clarified on the basis of the calculated excitation energies, oscillator strengths and changes of charge distribution accompanying electronic transitions. The nature of the second excited state of aniline is discussed in detail, in connection with the problem of electron transfer.

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*Electronic Spectra of Substituted Aromatic Hydrocarbons. II. Naphthols and Naphthylamines**

By Hiroaki BABA and Satoshi SUZUKI

(Received July 22, 1960)

The effect of substitutions on the electronic spectrum of a conjugated molecule depends upon the positions at which the substituents are attached to the molecule. With naphthalene, there is a noticeable difference between the spectral changes caused by substitutions at α- and β-positions. Several theoretical studies have been made to account for this interesting phenomenon[1]. The treatments, however, were limited to the framework of the LCAO molecular orbital (MO) theory in its simplest form, because substituted naphthalenes are complex molecules which have only low symmetry or none at all.

In the present study, the ultraviolet absorption spectra of naphthols and naphthylamines have been newly measured, and the effects of hydroxyl and amino substitutions upon the naphthalene spectrum have been examined on the basis of a calculation which was carried out according to the same method as that used in the preceding paper[2] (hereafter referred to as I).

Experimental

Materials.—α-Naphthol was recrystallized from ligroin, and β-naphthol from water and ligroin. Both were further purified by vacuum sublimation; m. p. 93.0~93.5°C and 119.0~119.5°C, respectively. α-Naphthylamine and β-naphthylamine were repeatedly recrystallized from ligroin, and were sublimed in vacuo; m. p. 48.5~49.0°C and 110.0~110.5°C, respectively. Each of the four samples was subjected to vacuum sublimation whenever it was used for a measurement.

Isooctane (2,2,4-trimethylpentane; Enjay Co., Inc., U. S. A.) was carefully purified by distillation and by being passed through a chromatography tube filled with dried silica-gel powder. The isooctane thus purified is transparent down to 200 mμ.

Measurement of Spectra and Results.—Ultraviolet absorption spectra were measured at controlled

* Read in part at the Symposium on Electronic States in Molecules, held by the Chem. Soc. Japan, Oct. 1958. (See Abstract of the Meeting, p. 73).

1) D. Peters, *J. Chem. Soc.*, 1957, 646, 1993, 4182; K. Nishimoto and R. Fujishiro, This Bulletin, 32, 445 (1959); R. Fujishiro and K. Nishimoto, Abstract of the Symposium on Electronic States in Molecules, held by the Chem. Soc. Japan, Sept. 1959, p. 14.

2) H. Baba, This Bulletin, 34, 76 (1961).

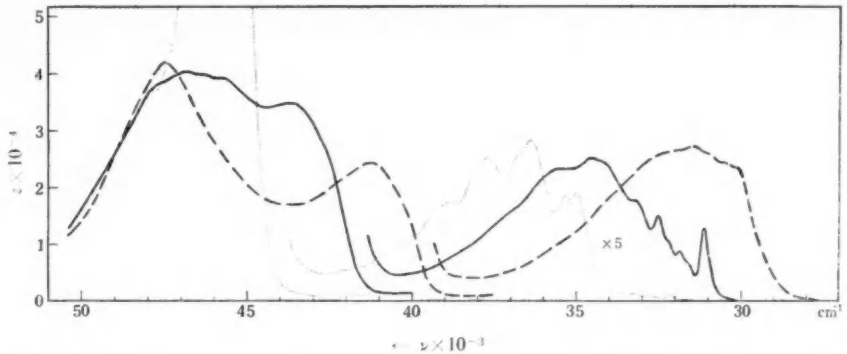

Fig. 1. Ultraviolet absorption spectra of α-naphthol (——), α-naphthylamine (----) and naphthalene (·····) in isooctane.

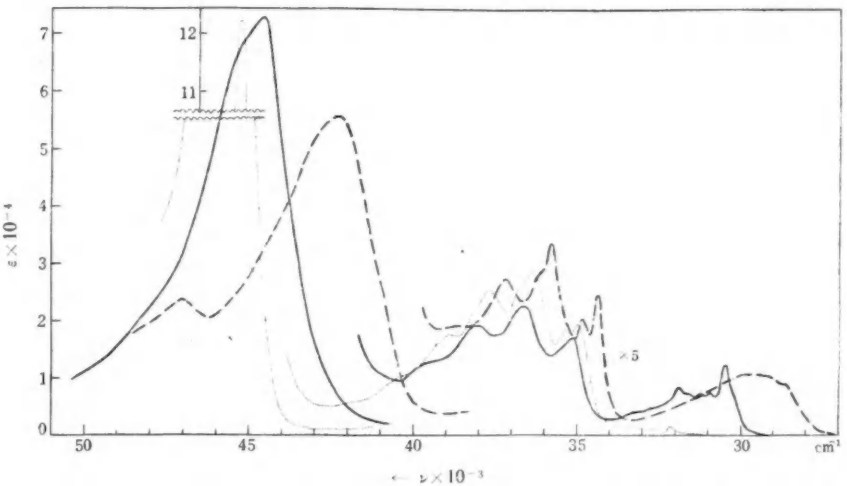

Fig. 2. Ultraviolet absorption spectra of β-naphthol (——), β-naphthylamine (----) and naphthalene (·····) in isooctane.

temperatures with a Hitachi quartz spectrophotometer of type EPU-2A. Attention was paid to the width of the slit so that the effective band width of the exit beam came to be sufficiently narrow as compared with the width of the absorption bands. Silica cells of 10 mm. and 2.5 mm. lengths were used, each of which was fitted with a ground-glass stopper. It was confirmed that Beer's law holds for all the substances in isooctane over the range of concentrations (10^{-4}~10^{-5} mol./l.) used in the present measurement.

The absorption spectra of the α- and β-derivatives are shown, respectively, in Figs. 1 and 2. The spectra were observed at 20°C except for that of α-naphthylamine, which was obtained at 17.5°C. In the figures the spectrum of naphthalene[3] is also given for ready comparison.

3) American Petroleum Institute Research Project 44, Ultraviolet Spectral Data, Serial No. 640, 654.

Calculation

Calculations have been made for α-, β-naphthols and α-, β-naphthylamines by following the same procedure as in I. Various theoretical quantities are at first presented as functions of the parameter δ_X; and then the values of the quantities for naphthols and naphthylamines are derived by assuming δ_O and δ_N to

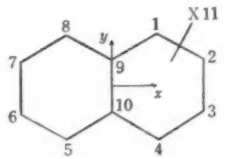

Fig. 3.

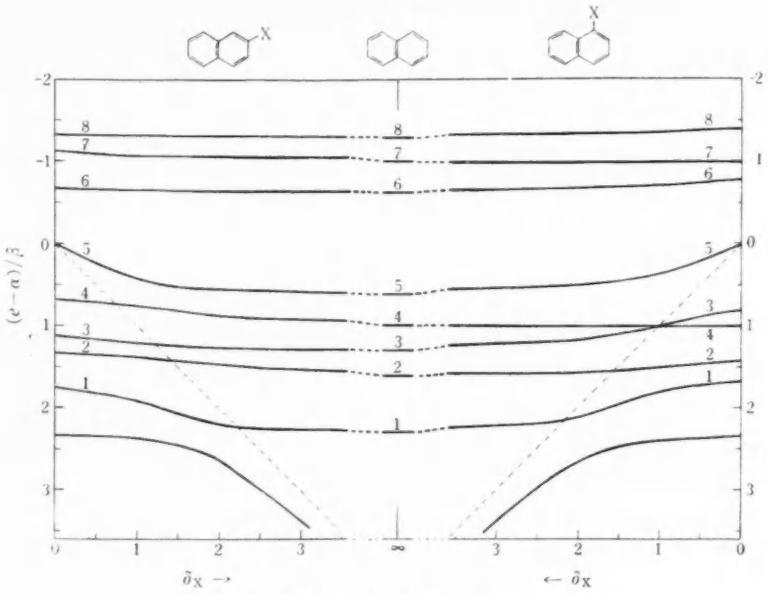

Fig. 4. Relation of MO energies to δ_X.

be equal to the corresponding parameter values determined in I for phenol and aniline. The notation used in this paper is the same as in I.

Molecular Orbitals.—The MO's of the parent hydrocarbon, naphthalene, are designated as $\phi_1^0, \phi_2^0, \cdots\cdots$ in the sequence of ascending energy. Among these the following MO's are primarily associated with the lower electronic transitions[4].

$$\phi_4^0 = a(\chi_2+\chi_3+\chi_6+\chi_7) - a(\chi_9+\chi_{10}), \qquad e_4^0 = \alpha+\beta \tag{1a}$$

$$\phi_5^0 = b(\chi_1-\chi_4+\chi_5-\chi_8) + c(\chi_2-\chi_3+\chi_6-\chi_7), \qquad e_5^0 = \alpha+0.6180\beta \tag{1b}$$

$$\phi_6^0 = b(\chi_1+\chi_4-\chi_5-\chi_8) - c(\chi_2+\chi_3-\chi_6-\chi_7), \qquad e_6^0 = \alpha-0.6180\beta \tag{1c}$$

$$\phi_7^0 = -a(\chi_2-\chi_3-\chi_6+\chi_7) + a(\chi_9-\chi_{10}), \qquad e_7^0 = \alpha-\beta \tag{1d}$$

where $a=0.4082$, $b=0.4253$, $c=0.2629$; χ_p is the pth atomic orbital (see Fig. 3 for the numbering of the positions); the superscript zeros refer to the parent hydrocarbon.

The energies of the ground-state MO's and of the lower excited MO's for the monosubstituted naphthalenes are plotted against δ_X in Fig. 4.

Configuration Interaction.—With naphthalene, configurations V_{46}^0 and V_{57}^0 belong to B_{3u}, and V_{47}^0 and V_{56}^0 to B_{2u} species of the symmetry group D_{2h}[5]. According to the simple LCAO treatment, the configuration V_{46}^0 and V_{57}^0 are degenerate, but V_{47}^0 and V_{56}^0 are not (cf. Eqs. 1a—1d). To a first approximation, interaction is included only between the degenerate configurations, V_{46}^0 and V_{57}^0[6]. The wave functions thus obtained for the lower excited states of naphthalene are shown in Table I. Using the observed excitation energies, given in Table I, one obtains

Table I. Excited states of naphthalene

Symmetry	Wave function	Observed excitation energy* (eV.)
B_{3u}^-	$\frac{1}{\sqrt{2}}(V_{46}^0-V_{57}^0)$	3.99
B_{2u}	V_{56}^0	4.51
B_{3u}^+	$\frac{1}{\sqrt{2}}(V_{46}^0+V_{57}^0)$	5.62

* Taken from Ref. 3.

$$E(V_{46}^0) = E(V_{57}^0) = \frac{1}{2}\{W^0(B_{3u}^-) + W^0(B_{3u}^+)\}$$
$$= E(V_6^0) + 4.80 \text{ eV}.$$
$$E(V_{56}^0) = E(V_6^0) + 4.51 \text{ eV}.$$

4) R. Pariser, *J. Chem. Phys.*, **24**, 250 (1956).

5) The group-theoretical notation is the same as that used in G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Company, Inc., New York (1945), p. 108. The x and y axes are chosen as in Fig. 3 and the z axis is perpendicular to the molecular plane.

6) M. J. S. Dewar and H. C. Longuet-Higgins, *Proc. Phys. Soc. (London)*, **A67**, 795 (1954).

Hence it follows from Eq. 2 of I

$$\beta^0_{4\to8}=\beta^0_{5\to7}=-2.97\text{ eV.}=\beta^0(\mathrm{B_{2u}}) \quad (2a)$$

$$\beta^0_{5\to6}=-3.65\text{ eV.} \quad (2b)$$

With the naphthalene derivatives, even the energies of V_{46} and V_{57} are no longer equal. In this calculation, only the interaction is taken into account between those configurations of the derivatives which are degenerate in the parent hydrocarbon. Thus the interaction of V_{46} and V_{57} is included; on the other hand, V_{56} is assumed to represent the wave function for an excited state without mixing with any other configurations. The energies of these configurations are obtained from Eq. 2 of I on the assumption that $\beta_{4\to8}=\beta_{5\to7}=\beta^0(\mathrm{B_{2u}})$ and $\beta_{5\to6}=\beta^0_{5\to6}$.

The calculation of the matrix element $\{V_{46}\mid V_{57}\}$ is made in exactly the same way as in I. The integral values used in the present calculation are the same as those used in I. As a result, it follows that

naphthalene, $\{V^0_{46}\mid V^0_{57}\}=0.918$ eV.

α-derivative, $\{V_{46}\mid V_{57}\}=0.866$ and 0.782 eV.

β-derivative, $\{V_{46}\mid V_{57}\}=0.824$ and 0.693 eV.

where the values for each derivative correspond, respectively, to the paramater values $\delta_X=2.0$ and 1.2.

State Energies.—The calculated energies of the excited states are shown in Fig. 5 as functions of δ_X; the observed excitation energies of naphthalene, naphthols and naphthylamines are also indicated in the figure. In the parent hydrocarbon, naphthalene, the calculated and observed energies of the $\mathrm{B_{2u}}$ state are, of course, in accord with each other. The energies of the $\mathrm{B^-_{2u}}$ and $\mathrm{B^+_{2u}}$ states are calculated, respectively, to be 3.89 and 5.72 eV., both being in good agreement with the observed excitation energies (see Table I). This may be regarded as a proof that the used integrals are of suitable values.

The monosubstituted naphthalenes have no symmetry, apart from their symmetry with respect to the molecular plane. However, the wave functions or energy levels of the derivatives may be denoted by the analogy of the notation for the corresponding quantities of the parent hydrocarbon. Thus, for example, the lowest excited state of the derivatives will be designated as $(\mathrm{B^-_{2u}})$, where the symbol of the symmetry type for the parent hydrocarbon is inclosed in parentheses.

Oscillator Strengths.—Oscillator strengths, f, are calculated from Eq. 12 of I. Plots of f_{calc} vs. δ_X are given in Fig. 6. It may be noted that f_{calc} values for the transitions to $\mathrm{B^-_{2u}}$, $\mathrm{B_{2u}}$ and $\mathrm{B^+_{2u}}$ states in naphthalene are, respectively, 0, 0.52 and 2.14, corresponding f_{obs} values being 0.002, 0.11 and 1.70[7].

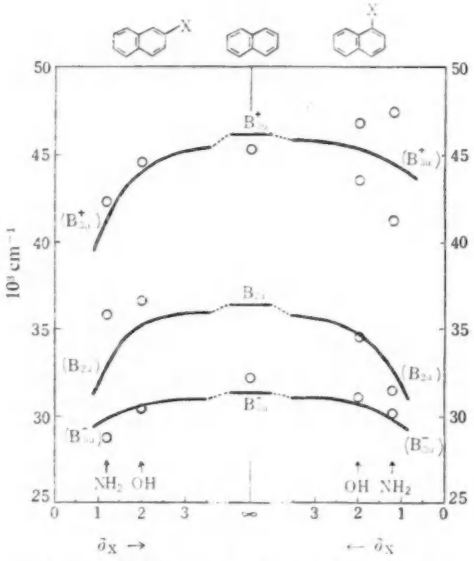

Fig. 5. Relation of the energies of the excited states to δ_X. The observed energies are represented by circles.

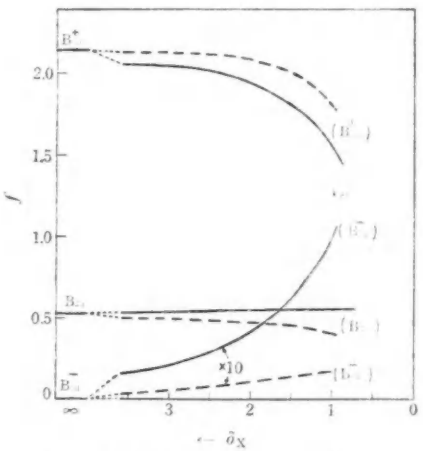

Fig. 6. Relation of f values to δ_X.
——, α-derivative; ----, β-derivative.

Summary of Calculation.—As the most appropriate values for the Coulomb integral parameters of the oxygen and nitrogen atoms,

7) H. B. Klevens and J. R. Platt, *J. Chem. Phys.*, **17**, 470 (1949).

TABLE II. EXCITED STATES OF NAPHTHOLS AND NAPHTHYLAMINES

	State	Wave function	Excitation energy (cm^{-1})		f		Δq_X
			calc.	obs.	calc.	obs.*	
	(B_{3u}^-)	$0.591V_{46}-0.807V_{57}$	30800	31100	0.042	0.016	−0.038
α-Naphthol	(B_{2u})	V_{56}	34800	34570	0.55	0.102	−0.049
	(B_{3u}^+)	$0.807V_{46}+0.591V_{57}$	45400	43570 46820	1.94	0.328 0.892	−0.010
	(B_{3u}^-)	$0.766V_{46}-0.643V_{57}$	30600	30470	0.011	0.0211	−0.056
β-Naphthol	(B_{2u})	V_{56}	35200	36600	0.48	0.0811	−0.043
	(B_{3u}^+)	$0.643V_{46}+0.766V_{57}$	44100	44580	2.08	1.06	−0.049
	(B_{3u}^-)	$0.502V_{46}-0.865V_{57}$	29900	30100	0.082	0.13	−0.13
α-Naphthyl-amine	(B_{2u})	V_{56}	32700	31500	0.55		−0.14
	(B_{3u}^+)	$0.865V_{46}+0.502V_{57}$	44500	41250 47440	1.68	0.34 0.82	−0.011
	(B_{3u}^-)	$0.778V_{46}-0.628V_{57}$	29900	28740	0.016	0.033	−0.13
β-Naphthyl-amine	(B_{2u})	V_{56}	33000	35790	0.43	0.10	−0.16
	(B_{3u}^+)	$0.628V_{46}+0.778V_{57}$	41300	42340	1.91	0.86	−0.14

* For the details of the determination of the observed f values see Ref. 8.

$\delta_O=2.0$ and $\delta_N=1.2$ were obtained in I. Application of these values to the case of the naphthalene derivatives leads to the results summarized in Table II, where the changes of the π-electron density, Δq_X, accompanying the electronic transitions are also given. The observed excitation energies and oscillator strengths are cited in the table.

In connection with the Δq_X values it is instructive to know the charge distribution in the ground state. Thus, from the ground-state MO's corresponding to $\delta_X=1.2$, quantities related to the charge distribution in the ground state were derived for naphthylamines. The results are collected in the molecular diagrams of Fig. 7, in which the analogous diagram for aniline is shown for the sake of comparison.

Discussion

Inspection of Fig. 4 reveals several features of the MO's of the naphthalene derivatives. In the α-derivative, orbital energies e_4 and e_7 are completely identical with e_4^0 and e_7^0, respectively, regardless of the value of δ_X; e_3 is raised with decreasing magnitude of δ_X, and consequently the sequence of the heights of e_3 and e_4 is reversed at $\delta_X=1$; e_5 is most affected by the α-substitution. In the β-derivative e_4 is strongly influenced by the substitution, while e_3 remains almost unaltered. When δ_X is large e_5 is little changed upon the β-substitution, but it is considerably affected by a substituent with a small magnitude of δ_X, i.e., by a strongly conjugating substituent. The behaviors of the orbital energies in the α- and β-derivatives may, at least in part, be understood in terms of the coefficients of the atomic orbitals in the MO's of the parent hydrocarbon (cf. Eqs. 1a—1d).

Regarding the wave functions of the excited states, it is to be noted that the degrees of configuration mixing in the wave functions of the ($B_{3u}^{\pm}$) states are appreciably changed by the substitutions.

Before proceeding to a discussion of the excitation energies, mention should be made of the spectra shown in Fig. 1. In the spectrum of α-naphthol, several minor peaks are present on the lower frequency side of the 34570 cm^{-1} band. In the light of the spectrum of naphthalene it is reasonable to regard these peaks as showing a fine structure of a definite electronic band which corresponds to the lowest frequency band of the parent hydrocarbon. No analogous band is found, at first sight, in the α-naphthylamine spectrum. However, the 31500 cm^{-1} band of α-naphthylamine exhibits relatively high extinction at the shoulder of 30100 cm^{-1}, as compared with the corresponding bands of α-naphthol and naphthalene. In view of this fact, the present authors tentatively assumed that the band in question is hidden under the more intense band of 31500

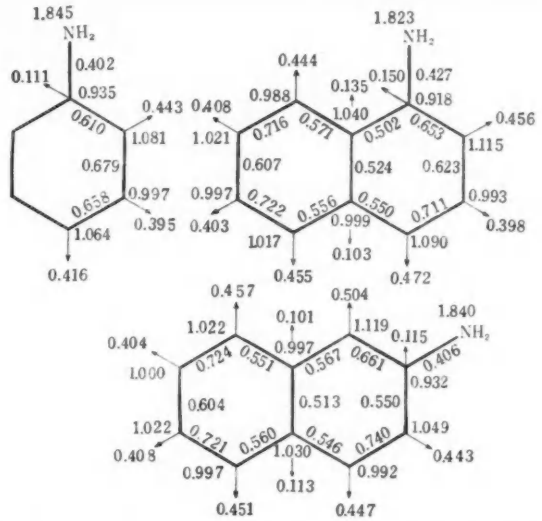

Fig. 7. Molecular diagrams for aniline, α-naphthylamine and β-naphthylamine. The π-electron density, π-bond order and free valence are shown in the usual manner for each molecule.

cm^{-1} in the neighborhood of the said shoulder.

α-Naphthol has two absorption bands (ν_{max} =43570 and 46820 cm^{-1}) in the higher frequency region, which are not fully separated from each other. It has been observed that, when a hydrogen bond is formed between α-naphthol and dioxane, these bands exhibit quite different behaviors: that is, the lower frequency band is displaced to the red and the other to the blue[8]. This observation conclusively indicates that the bands under consideration are due to two distinct electronic transitions.

The calculated excitation energies for the (B_{1u}^-) and (B_{2u}) states of the α-derivatives are in good accord with the observed. A difficulty arises in the fact that two levels are observed near the calculated (B_{1u}^+) level of the α-derivatives. A tentative explanation for this will be given below.

According to Pariser's calculation for naphthalene, there exists a B_{1g}^+ state slightly below the B_{1u}^+ state[4]. A plus state in general favors the transition from the ground state[4], but in the case of the B_{1g}^+ state the transition is forbidden, because $A_g \rightarrow B_{1g}$ is not allowed by the selection rule. To a first approximation, the B_{1g}^+ state is represented by $(1/\sqrt{2})(V_{56}^0 + V_{78}^0)$. As has already been shown, ϕ_7^0 and ϕ_8^0 are profoundly influenced by the α-substitution, so that the B_{1g}^+ state will be subjected to a considerable distortion. It is therefore probable that the B_{1g}^+ state comes to be allowed in the α-derivatives, and that a fairly strong interaction occurs between the (B_{1u}^+) and (B_{1g}^+) states to give two mixed states which can be assigned to the observed levels mentioned above. It seems reasonable to conclude that, of the two observed bands in question, the one of higher intensity, i.e., that of higher frequency, primarily corresponds to the (B_{1u}^+) state and the other to the (B_{1g}^+) state, for the transition to the B_{1u}^+ state is allowed even in the parent hydrocarbon.

Next, discussion will be turned to the excitation energies in the β-derivatives. There is a discrepancy between the calculated and observed energies of the (B_{2u}) state. It is generally accepted that the *p* band of naphthalene, which arises from the $A_g \rightarrow B_{2u}$ transition, is makedly shifted to the red by α-substitution, whereas it exhibits almost no shifts due to β-substitution[1]. The B_{2u} state of naphthalene is approximately represented by V_{56}^0. Also, for the coefficients of the atomic orbitals in ϕ_5^0 and ϕ_6^0, the relation $b^2 \gg c^2$ is seen to hold. Accordingly, so far as the behaviors of the *p* band are treated from the viewpoint of the perturbation theory, the calculation will lead to a result which is compatible with the observation. This is substantiated by the

8) H. Baba and S. Suzuki, to be published in *J. Chem. Phys.*

results of Peters' perturbation treatment[1]. However, quite a different situation may be produced for strongly conjugating substituents, to which the perturbation theory fails to apply. In fact, in cases $\delta_X < 2$ the orbital energy e_5 is noticeably raised even in the β-derivatives, and hence the calculated excitation energy for $\phi_5 \rightarrow \phi_6$ becomes considerably smaller than the observed. This discrepancy is the most serious is the most serious difficulty involved in the present calculation.

From the spectra of Figs. 1 and 2, the effect of substitutions on the band intensities may be summarized as follows: the intensity of the transitions to the (B_{3u}^-) state is greatly enhanced, while that of the transition to the (B_{1u}^+) state is lowered; the transition to the (B_{2u}) state is subject to only a slight change in its intensity. These remarks are applicable to each of the α- and β-derivatives. It may be said that the f_{calc} values account, at least qualitatively, for the observed intensity variations due to the substitutions.

One may predict from the calculation of Δq_X that all transitions in both the α- and β-derivatives are accompanied by an increase of the positive charge at the substituent, and that the increment of the charge is extremely small as regards the transition to the (B_{1u}^+) state of the α-derivatives. This prediction has been verified in its essential points by experimental studies of the hydrogen bonding effect on the spectra of naphthols and naphthylamines[2].

By comparing the diagrams of Fig. 7, which are based on the molecular orbital method, with those obtained by the valence bond method[9,10], it is found that the two theoretical methods lead to essentially the same results in respect of both the charge distributions and the bond orders for aniline and the amines. It may be worthy of note that the π-electron densities at the nitrogen atoms are in the order

aniline> β-naphthylamine> α-naphthylamine

The present calculation is based on the assumption of the transferability of the parameters δ_N and δ_O from the benzene derivatives to the naphthalene derivatives. This assumption is seen to be reasonable on the inspection of Table II and Fig. 5.

Summary

The ultraviolet absorption spectra of α-, β-naphthols and α-, β-naphthylamines have been newly measured down to 200 mμ. On the basis of a calculation which was carried out in the same manner as in the preceding paper, the effect of substitutions at α- and β-positions upon the spectrum of napthalene has been explained and the assignment of the observed absorption bands has been made. It is suggested that, upon substitution at the α-position, the $A_u \rightarrow B_{1u}^+$ band of naphthalene splits into two electronic bands because of the interaction of the B_{1u}^+ state with a B_{1g}^+ state. Molecular diagrams are given for naphthylamines and for aniline.

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9) B. Pullman, *Bull. soc. chim. France*, **1948**, 533.
10) R. Daudel and M. Martin, ibid., **1949**, 83.

Thermal Decomposition of Potassium Chlorate

By Shōtarō TOBISAWA

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The thermal decomposition of potassium chlorate has been investigated mostly by measuring the volume of oxygen gas evolved[1-4]. The present author has studied this reaction from the viewpoint of the loss in weight (x), due to oxygen gas released in the progress of the decomposition. The measurement of loss in weight was made at definite intervals of 45 sec. with a thermal balance of automatic recording type. Plots of dx/dt against time (t) were obtained accurately.

Experimental

Commercial guaranteed potassium chlorate was recrystallized four times from water. A single crystal and a polycrystal were selected from the recrystallized samples under a microscope. A powdered sample was obtained by carefully squeezing the recrystallized sample in an agate mortar with a pestle. The detail of the thermal balance was already described in a previous report[5]. This balance was modulated to be able to indicate distinct differences of 0.022 mg. on a recording chart.

Results

When the temperature of the powdered sample was raised at constant rate, 250°C per hour, it decomposed at 500°C, evolving oxygen gas. Although the measurements were made for the powdered samples of different weights and also at different rates of heating, these samples decomposed at the same temperature of 500°C which was higher than the decomposition temperature obtained by Vitoria[6]. Since the melting point of potassium chlorate has been found to be 352°[7] or 356°C[6], it is reasonable to consider that the thermal decomposition of potassium chlorate takes place in liquid state.

The kinetic measurements were made at several temperatures above 500°C. The reactant sample could reach these constant temperatures within five minutes. Fig. 1 shows the plots

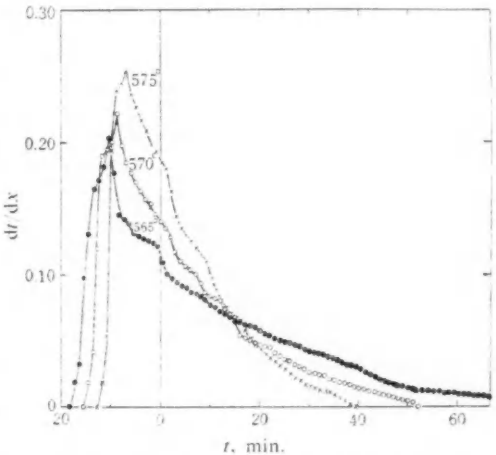

Fig. 1. Plots of dx/dt against time for the powdered samples (12.0 mg. in weight).

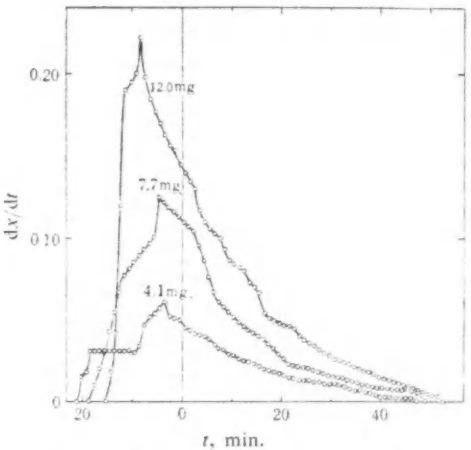

Fig. 2. Plots of dx/dt against time for the powdered samples at 570°C.

of dx/dt against t for the powdered samples of 12.0 mg. at 565, 570 and 575°C, respectively. The time of zero in Fig. 1 was set at the point where half of the weight of the sample was decomposed. In the figure, the acceleratory period is extremly short in comparison with the decay period. From the curves of dx/dt

1) J. Scobai, *Z. physik. Chem.*, **44**, 319 (1903).
2) W. Farmer and J. B. Firth, *J. Chem. Soc.*, **125**, 82 (1924).
3) C. E. Otto and H. S. Fry, *J. Am. Chem. Soc.*, **46**, 272 (1924).
4) A. Glasner and L. Weidenfeld, ibid., **74**, 2464 (1952).
5) S. Tobisawa, This Bulletin, **32**, 1173 (1959).
6) A. P. Vitoria, *Anales soc. espan. fis. quim.*, **27**, 787 (1929); *Chem. Abstr.*, **24**, 773 (1930).
7) S. Tobisawa, to be published.

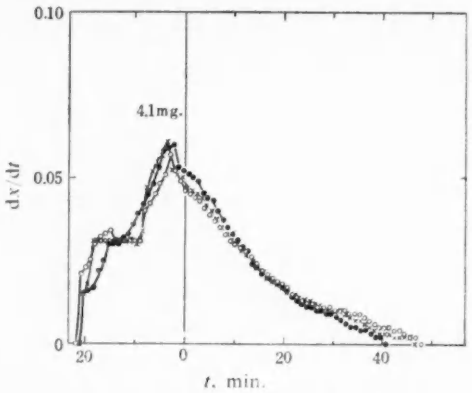

Fig. 3. Plots of dx/dt against time at 570 C.
—○—: Single crystal,
—●—: Polycrystal,
—×—: Powdered sample.

against t at the same temperature in Fig. 2, it is seen that, as the weight of the sample decreases, the acceleratory period becomes long and the shape of the curve of dx/dt against t in the acceleratory period becomes complicated. Fig. 3 shows the plots of dx/dt against t for the single crystal, the polycrystal and the powdered sample, all in the same weight of 4.1 mg. at the same temperature, 570°C. In the figure, the curves of dx/dt against t for the three samples show different shapes in the acceleratory period, while the curves in the decay period show analogous shapes. In each measurement, total losses in weight, due to the exhausted decomposition, agreed with the amount of oxygen calculated from the equation, $2KClO_3 = 2KCl + 3O_2$, within the error of about one per cent.

Discussion

As shown in Figs. 1, 2 and 3, each curve of dx/dt against t shows a complicated shape, and such complication tends to disappear as the decomposition progresses. It has been reported by Otto et al.[7] that the reaction, $2KClO_3 \rightarrow 2KCl + 3O_2$, is a monomolecular reaction. Glasner et al.[4] have also stated that the decomposition at high temperature is of the first order. However, as is evident from Figs 1, 2 and 3, the thermal decomposition of potassium chlorate is so complicated that a rate-equation can not be determined.

In a microscopic study of the sample undergoing the thermal decomposition, zig-zag bubbles of oxygen gas were observed in the liquid. Moreover, by visual observation of a reaction vessel at the end of the experiment, specks which were considered to be owing to the splashing of the liquid, were recognized along the wall. The bubbling of gas causes the splashing of the liquid. On the liquid-phase decomposition of potassium perchlorate, Bircumshaw et al.[8] have stated that the composition of the liquid which consists of perchlorate, chlorate and chloride, will not be constant on account of the spreading of the liquid along the tube, owing to bubbling, and thus variations in the rate of evolution of gas may be expected, depending on how much splashing takes place. On the thermal decomposition of potassium chlorate, it has been known that the reaction system consists of chlorate, chlorite, perchlorate and chloride, and that the chlorate, the chlorite and the perchlorate convert into chloride with the evolution of oxygen gas[9]. The bubbling and splashing under such a complicated condition will take place very irregularly. The complication of the curves of dx/dt against t may, therefore, be associated with the irregularities of the bubbling and splashing. As the decomposition progresses, the bubbling and splashing will become difficult to take place on account of the accumulation of chloride in the liquid. Consequently, the complication of the curves of dx/dt against t may be expected to disappear.

Summary

The curves of dx/dt against t were obtained with accuracy; in consequence, the complication of the curves appeared, and the complication may be associated with the irregularities of the bubbling and splashing.

The author is particularly indebted to Professor Y. Nomura for his suggestion and encouragement throughout this work. Thanks are also due to Mr. S. Shimoyama for his kind assistance.

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9) H. Osada, *J. Ind. Explosives Soc. Japan*, **15**, 324 (1954).

*Infrared Spectra of Troponoid Compounds. II. Absorption Band of O–H Stretching Vibration in Some Tropolones**

By Yusaku IKEGAMI

(Received February 10, 1960)

In the previous report[1], it was shown that the absorption bands assignable to O–H stretching vibration in tropolone (I) appear at around 3210 cm^{-1} in solid and around 3140 cm^{-1} in solution or gaseous state, indicating the characteristic properties in absorbing at a lower wave number in dilute solution or gaseous state than in solid. This fact has been explained[1-3] on the basis of the intermolecular or intramolecular hydrogen bonding in tropolone, but the nature of these bands was not studied in detail. In this paper, the examinations were made on O–H stretching absorption bands of tropolone, by using a calcium fluoride prism, to see how the absorption bands changed with different concentrations and states. The same examinations were also made on 4-isopropyltropolone (hinokitiol) (II) and 3-bromotropolone (III).

Experimental

Infrared absorption spectra were measured with a Perkin-Elmer model 21 infrared spectrophotometer with a calcium fluoride prism. The solid spectra were obtained by potassium bromide disk or sandwich method, and a cell of 0.109, 0.508, 11.10 or 50.30 mm. thick with potassium chloride windows was used to obtain solution spectra.

Results and Discussion

Fig. 1 shows the infrared spectra of tropolone in the region of 3600～2600 cm^{-1}, measured for solid, liquid and solution in carbon tetrachloride, and shows that there are more absorption bands in this region than had been expected. It also reveals the change in the spectrum accompanying variation of the concentration in solution and of the phase. The two bands in the ranges of 3051～3049 and 3020～3003 cm^{-1} in these spectra correspond to the C–H stretching vibration in the seven-membered ring, which appear with comparative regularity in many of the troponoids[4]. Absorption bands other than these two must be those of O–H stretching vibration in respective states since corresponding bands do not appear in 2-deuteroxytropone[5] and metal tropolonate[4].

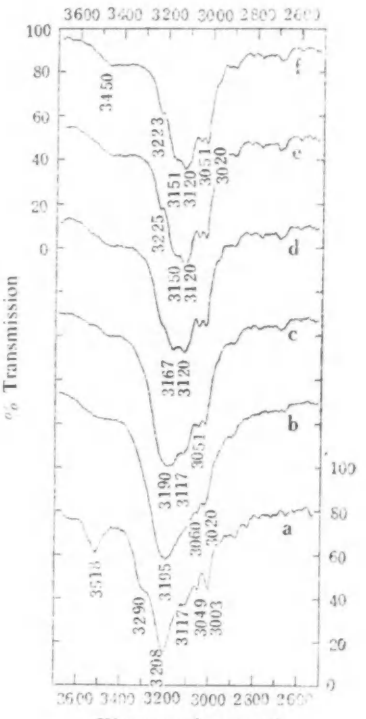


Fig. 1. Infrared spectra of tropolone in the states of solid, liquid and carbon tetrachloride solution (3600～2600 cm^{-1} range): a; solid (crystalline film), b; liquid, c; ca. 1.5 mol./l. in CCl_4 (0.109 mm. thickness), d; 0.29 (0.508), e; 0.014 (11.10), f; 0.0029 (50.30).

From the spectra shown in Fig. 1, the following characteristics can be pointed out. a) When measured in the most dilute solution shown in Fig. 1 f, there is no sharp absorption

* A part of this work was presented at the 10th Annual Meeting of the Chemical Society of Japan, April 4, 1957.

1) Part I: S. Kinumaki, K. Aida and Y. Ikegami, *Sci. Repts. Research Inst. Tohoku Univ., Ser.* **A, 8**, 263 (1956).

2) K. Kuratani, M. Tsuboi and T. Shimanouchi, This Bulletin, **25**, 250 (1952).

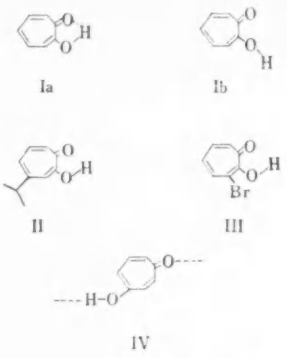
3) H. P. Koch, *J. Chem. Soc.*, 1951, 512.

4) Y. Ikegami, unpublished data.

5) Y. Ikegami, This Bulletin, **34**, 94 (1961).

and there are bands at 3151 and 3223 cm^{-1} besides the strongest one at 3120 cm^{-1} and a broad band at 3500~3300 cm^{-1}. b) The O-H stretching absorption is dependent of the concentration in solution, although it had been reported that the spectrum is independent[2], and the bands at 3151 and 3223 cm^{-1} increase their intensity gradually with increasing concentration, which finally merge into the comparatively broad absorption at 3195 cm^{-1} in liquid. c) The spectrum in solid state exhibits shoulders at 3117 and 3290 cm^{-1}, besides the strongest band at 3208 cm^{-1}, and a distinct band at 3518 cm^{-1}. The spectrum obtained in gaseous state[1] is the same as that of Fig. 1 f.

Such characters of the O-H stretching absorption band in dilute solution are not essentially different from those of chelated hydroxyquinones[6] and enolized β-diketones[7] possessing a conjugated chelate system, and can be taken as the characteristics indicating tropolone structure. It is seen from Fig. 1 that the absorption bands shift to the higher wave number side as the concentration increases and as the compound transits liquid or solid. On the other hand, the absorption band at 1618 cm^{-1} in solution appears at a wave number 5 cm^{-1} higher than that in solid[2]. This is contrary to the direction of the shift of $\nu_{C=O}$ anticipated from that of ν_{O-H} in the hydrogen bonding of -O-H···O=C type, and then the shift of O-H stretching absorption band can not be explained merely by the strength of hydrogen bonding in this type. Considering the fact that the direction of the shift of C=O stretching absorption band in tropolone according to changes in the states agrees with that in tropone[1], it is assumed that the cycloheptatrienone part in tropolones interacts in a manner similar to that in the case of tropone[7] and the intramolecular



hydrogen bonding is weakend by this interaction. Kuratani et al.[2] assumed a dimer form for tropolone in the solid state. However, a wave number 3208 cm^{-1} in tropolone is approximately 700 cm^{-1} higher than that in

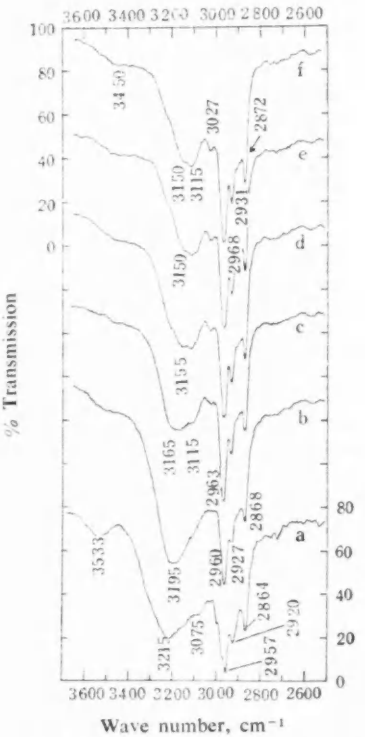


Fig. 2. Infrared spectra of 4-isopropyltropolone in the states of solid, liquid and carbon tetrachloride solution (3600~2600 cm^{-1} range): a; solid (crystalline film), b; liquid, c; ca. 1.2 mol./l. in CCl_4 (0.109 mm. thickness), d; 0.29 (0.508), e; 0.014 (11.10), f; 0.0029 (50.30).

6) D. Hadzi and N. Sheppard, *Trans. Faraday Soc.*, **50**, 911 (1954).

7) S. Bratoz, D. Hadzi and G. Rossmy, ibid., **52**, 464 (1956).

8) Unpublished data. Infrared spectra of tropone in the region of 1700~1500 cm^{-1} were measured in the states of vapor, liquid and solutions in various solvents. Two strong absorption bands in this region indicated the following wave-numbers, e. g.

vapor	1651 cm^{-1}	1613 cm^{-1}
in *n*-heptane	1645 cm^{-1}	1602 cm^{-1}
in acetonitril	1634 cm^{-1}	1585 cm^{-1}
in ethanol	1633 cm^{-1}	1574 cm^{-1}
pure liquid	1634 cm^{-1}	1580 cm^{-1}.

Also the shape of their bands in liquid tropone is similar to that in such a solvent as acetonitril, differing from it in the vapor state (cf. Ref. 1). From these facts, it is assumed that the tropone in liquid state associates by its polar character of B type as also shown in its large dipole moment (4.17D) (cf. Y. Kurita, S. Seto, T. Nozoe and M. Kubo, This Bulletin, **26**, 272 (1953)).

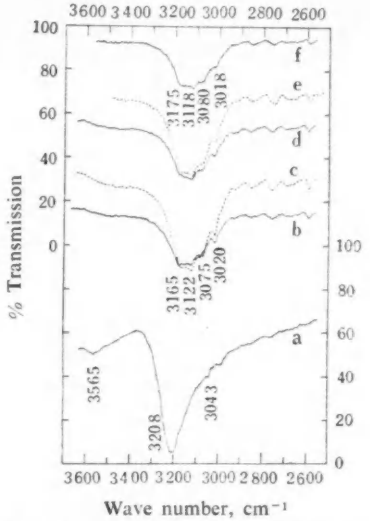


Fig. 3. Infrared spectra of 3-bromotropolone in the states of solid and carbon tetrachloride solution (3600~2600 cm^{-1} range): a; solid (KBr disk), b; 0.1 mol./l. in CCl_4 (0.508 mm. thickness), c; 0.01 (11.10), d; 0.005 (11.10), e; 0.002 (50.30), f; 0.001 (50.30).

4-hydroxytropone[9,10] (IV) (ν_{O-H}; 2920 (w.) and 2530 cm^{-1} (v. s., broad)) and 3-hydroxytropone[11], which form a strong intermolecular hydrogen bond in solid and show the higher melting points and less volatilities than those of tropolone. Therefore, even though solid tropolone forms a dimer, it is not easy to explain why the hydrogen bonding in the dimer form is weaker than that in hydroxytropones. In addition, a distinct band at 3518 cm^{-1} in Fig. Ia indicates the existence of unchelated O-H group as Ib type.

The absorption spectra of 4-isopropyltropolone (II) and 3-bromotropolone (III) are respectively indicated in Figs. 2 and 3. The spectra in Fig. 2 are essentially the same, with the exception of the bands due to isopropyl group, as the spectra in Fig. 1. 3-Bromotropolone is sparingly soluble in carbon tetrachloride. Its spectra in higher concentrations have not been measured, but the mode of change in the form of absorption can be learned similarly. It is therefore possible to discuss the absorption of these compounds in the same manner as in the case of tropolone.

The characters of O-H absorption bands above-mentioned will generally be observed in compounds possessing the skeletal structure of tropolone[12], but those forming a strong intermolecular hydrogen bonding such as 4- and 5-hydroxytropolones[13] and those showing extremely low intensity such as 3, 7-dibromo- and 3, 5, 7-tribromo-tropolones[14] do not show the typical O-H absorption band of tropolones.

Summary

Infrared spectra of tropolone, 4-isopropyltropolone and 3-bromotropolone in the solid, liquid and solution in carbon tetrachloride were measured with a calcium fluoride prism in the region of 3600~2600 cm^{-1}. The absorptions of O-H stretching vibration in these compounds in dilute solution are strongest at around 3120 cm^{-1} with numerous branches, and these bands shift gradually to the higher wave number side with 100~88 cm^{-1}, as the concentration increases and the compound transits to the liquid or solid state. This character was explained by the assumption that the tropolone skeleton has a stable chelate system and that the intermolecular action increases with the increase of concentration. In the solid state, a distinct band corresponding to the O-H group of Ib type was also observed at around 3540 cm^{-1}.

The author deserves to express his deep gratitude to Professor Susumu Kinumaki and Assistant Professor Koyo Aida for their unfailing guidance during the course of this work, and to Professor Tetsuo Nozoe and members of his laboratory for the donation of valuable samples.

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9) T. Nozoe, T. Mukai, Y. Ikegami and T. Toda, *Chem. & Ind.*, **1955**, 66; R. S. Coffey and A. W. Johnson, *J. Chem. Soc.*, **1958**, 1741.
10) Y. Ikegami, *J. Japan. Chem.* (*Kagaku-no-Ryoiki*), Extra No. 38, 46 (1959).
11) R. B. Johns, A. W. Johnson and M. Tisler, *J. Chem. Soc.*, **1954**, 4605.
12) Unpublished data. According to the results of spectral measurement made on about 40 kinds of tropolones, the O-H absorption bands appear in the region of 3260~3160 cm^{-1} (s.) in the solid state, and in the region of 3225~3095 cm^{-1} (m. or w.) in solution. Further, a very weak band generally appears in the region of 3640~3500 cm^{-1} in the solid.
13) Y. Kitahara, *Sci. Repts. Tohoku Univ., Ser.* **I**, **39**, 258 (1956).
14) K. Ogura and Y. Ikegami, *Bull. Chem. Research Inst. Non-Aqueous Solutions, Tohoku Univ.*, **9**, 23 (1959); Ref. 10, p. 60.

*Infrared Spectra of Troponoid Compounds. III. Tropolone and 2-Deuteroxytropone**

By Yusaku IKEGAMI

(Received February 10, 1960)

Absorption of O–H stretching vibration of tropolone (I) in solid, liquid and carbon tetrachloride solution was described in the preceding paper[1]. In the present paper the spectra of tropolone, chiefly in finger-print region, will be described. Infrared spectra of tropolone have been reported earlier by Koch[2], Kuratani[3], Kinumaki[4] and others, and its Raman spectrum by Imanishi and Ito[5], but only a few vibrations, such as those of C=O, C=C and C–H out-of-plane, have been assigned in the finger-print region. In order to clarify the absorption bands originating in C–O–H group in the spectrum of tropolone, an infrared spectrum of 2-deuteroxytropone (II) was measured and compared with that of I. On heating I with heavy water, a compound III, in which the deuterium atom had entered the seven-membered ring, was obtained and brief mention will be made of this compound. Further, some considerations were given to the spectrum of I in the finger-print region.

Results and Discussion

Comparison of the Infrared Spectra of 2-Deuteroxytropone and Tropolone.—2-Deuteroxytropone (II) was obtained by recrystallization of tropolone (I) from heavy water. The infrared spectra of I and II in carbon tetrachloride and carbon disulfide solutions are shown in Fig. 1, a and b. The presence of an absorption due to hydroxyl compound can not be denied in the spectrum of Fig. 1b but most of it is in the spectrum of II.

In the spectral curve of Fig. 1b, the O–H stretching absorption around 3150 cm^{-1} in 1a has shown drastic decrease of its intensity and a new absorption originating in the O–D bond has appeared at around 2400 cm^{-1}. This band has two peaks at 2400 and 2342 cm^{-1} and the shape of this band is similar to that of tropolone in which the O–H stretching absorption is not sharp even in the state of dilute solution. The ratio of the wave numbers of ν_{O-H} and ν_{O-D} is indicated in Table I together with values obtained in 3-bromo- and 3-methyl-tropolones. These values are in good agreement with the values (1.33~1.34) obtained by Keussler et al.[6] on deuteration of phenols

TABLE I. ν_{O-H}/ν_{O-D} VALUES FOR SOME TROPOLONES

Compounds		ν_{O-H} cm^{-1}	ν_{O-D} cm^{-1}	ν_{O-H}/ν_{O-D}
Tropolne	solid	3208	2385	1.345
	in CCl_4	3167	2400	1.320
		3120	2342	1.332
3-Bromotropolone	solid	3208	2390	1.342
3-Methyltropolone	solid	3202	2394	1.338

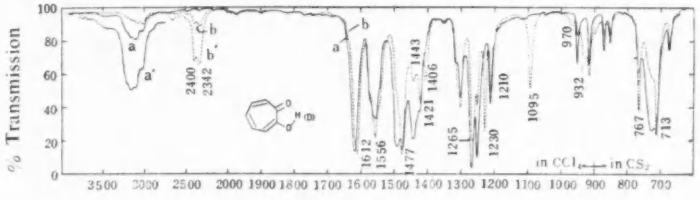

Fig. 1. Infrared spectra of tropolone (a: 3%, a': 10%) and 2-deuteroxytropone (b: 3%, b': 9%) in the solution of carbon tetrachloride (4000~900 cm^{-1} range) and of carbon disulfide (900~650 cm^{-1}) (0.12 mm. thickness).

* A part of this work was presented at the 10th Annual Meeting of the Chemical Society of Japan, April 4, 1957.

1) Part II: Y. Ikegami, This Bulletin, **34**, 91 (1961).
2) H. P. Koch, *J. Chem. Soc.*, **1951**, 512.
3) K. Kuratani, M. Tsuboi and T. Shimanouchi, This Bulletin, **25**, 250 (1952).
4) Part I: S. Kinumaki, K. Aida and Y. Ikegami, *Sci. Repts. Research Inst. Tohoku Univ., Ser.* **A. 8**, 263 (1956).
5) S. Imanishi and M. Ito, This Bulletin, **28**, 75 (1955); **29**, 632 (1956).
6) V. von Keussler und G. Rossmy, *Z. Elektrochem.*, **60**, 136 (1956).

possessing a conjugated chelate structure as tropolone.

In the region of 1700~650 cm^{-1} : — In this region, the absorption band at 1618 cm^{-1} in I shifts to the lower wave number side by 6 cm^{-1} in II, and a certain amount of difference is observed between I and II below 1500 cm^{-1}. New bands have appeared at 1406, 1230, 1095, 970 and 932 cm^{-1} in the spectrum of Fig. 1b. On the other hand, the absorption bands at 1490, 1444, 1251, 953 and 726 cm^{-1} in I do not appear in II, and the intensity of the absorption at 1267 cm^{-1} is weaker. These bands in Fig. 1a are considered to have some relation, either directly or comparatively closely, to the vibration of the C–O–H group.

Identification of absorption bands originating in the C–O–H group by conversion of hydroxyl to deuteroxyl compound has been reported already by Hadzi, Mecke and others in carboxylic acids[7], chelated hydroxyquinones[8], enolized β-diketones[9,10] and phenols[11]. These results point out that the distribution of absorption bands which shift by deuteration and their interpretation vary according to the shape of a molecule, even in the same C–O–H group. In the case of tropolone, a storng absorption band at 1490 cm^{-1} disappeared and a new band appeared at 1095 cm^{-1} (1086 cm^{-1} in solid) by deuteration, and these wave numbers are close to those which were assigned to the O–H and O–D deformation vibrations in enolized β-diketones (around 1435 and 1090 cm^{-1} respectively)[9]. Moreover, the other band which can be assigned to the O–D deformation vibration appeared at

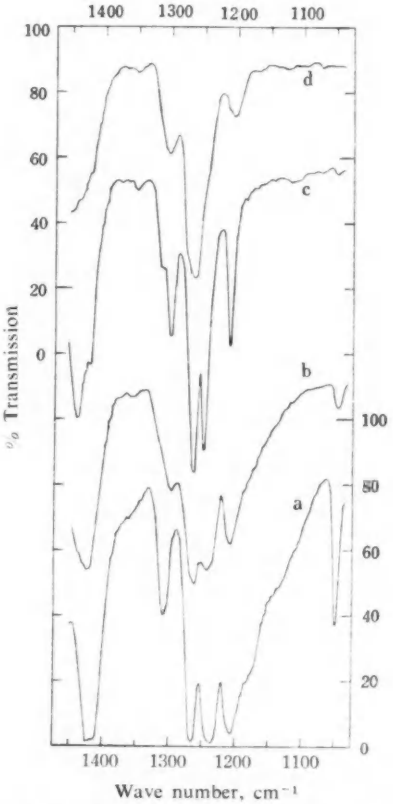

Fig. 2. Infrared spectra of tropolone in the states of solid (a), liquid (b), CCl_4 solution (c) and vapor (d) (1450~1050 cm^{-1} range).

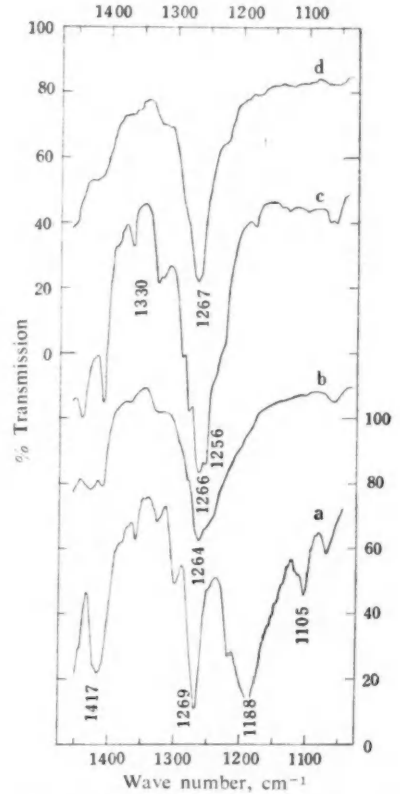

Fig. 3. Infrared spectra of 4-isopropyltropolone in the states of solid (a), liquid (b), CCl_4 solution (c) and vapor (d) (1450~1050 cm^{-1} range).

7) D. Hadzi and N. Sheppard, *Proc. Roy. Soc.*, **216A**, 247 (1953).
8) Idem., *Trans. Faraday Soc.*, **50**, 911 (1954).
9) S. Bratoz, D. Hadzi and G. Rossmy, ibid., **52**, 464 (1956).
10) R. Mecke and E. Funck, *Z. Elektrochem.*, **60**, 1124 (1956).
11) R. Mecke and G. Rossmy, ibid., **59**, 866 (1955).

932 cm^{-1} (896 cm^{-1} in solid) by deuteration, while the band at 1267 cm^{-1} weakened. These wave numbers are close to those of chelated hydroxyanthraquinones, in which two bands characteristic to the deuteroxyl group had been recognized at around 980 and 930 cm^{-1} [8]. Anyway, these facts indicate that the bands at 1490 and 1267 cm^{-1} in tropolone originate in the C–O–H group, although the definite assignments of these bands are indistinct.

It is clear that the bands at 1490 and 1267 cm^{-1} in Fig. 1a are related to the vibration of the C–O–H group, not only because these bands shift by deuteration but because 2-halotropones, which have no C–O–H group, do not have strong absorptions this wavenumber region[12]. The fact that the absorption at around 1267 cm^{-1} in tropolone has the character of O–H deformation is also understandable by comparing the spectra in solid, liquid, solution and gaseous states. The spectra in these states in the region of 1450~1050 cm^{-1} are shown in Fig. 2, and the spectra of 4-isopropyltropolone, for the comparison with those, are also shown in Fig. 3. From the spectra in Fig. 3, it is clear that the broad absorption

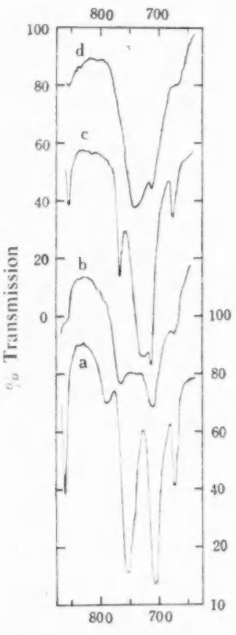

Fig. 4. Infrared spectra of tropolone in the states of solid (a), liquid (b), CS_2 solution (c), and vapor (d) (850~650 cm^{-1} range).

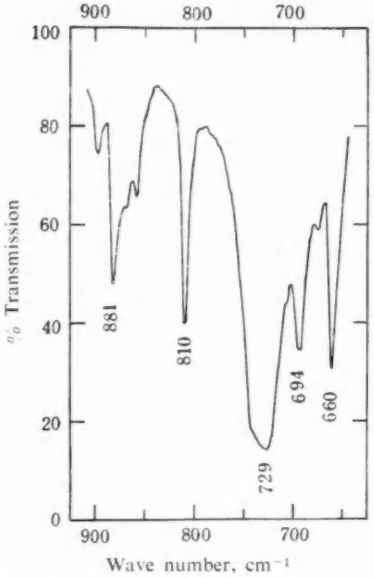

Fig. 5. Infrared spectrum of deuterated tropolone (III) in carbon disulfide (ca. 8%) (900~650 cm^{-1} range).

at 1188 cm^{-1} in solid has shifted to the higher wave number side, merging in the position at around 1265 cm^{-1} in other states. In the same manner, the broad absorption in the region of 1208~1100 cm^{-1} in solid tropolone (Fig. 2a) shifts to the higher wave number side in other states and is assumed to correspond to the strong absorption at 1265 cm^{-1} in the gaseous. The direction of such a shift of absorptions according to changes in the state agrees with the direction of the shift of δ_{O-H} anticipated from that of ν_{O-H} as stated in the preceding report[1].

The absorption bands which shift by deuteration are recognized at 1444, 1251 and 953 cm^{-1}, but these bands have also disappeared in the compound III, as will be described below. In these bands, the absorption at 1251 cm^{-1} is assumed to correspond to that at 1230 cm^{-1} in Fig. 1b, from their similar shape.

In the region of 800~700 cm^{-1}, there are three strong absorption bands in the state of solution. Of these, the band at around 720 cm^{-1} was assigned by Koch[2] and Kuratani et al.[3] to the out-of-plane vibration of hydrogen atoms in the seven-membered ring. On the other hand, Imanishi and Ito[5,13] assigned the Raman line at 743 cm^{-1} to the breathing vibration of the seven-membered ring. Moreover, the following considerations are possible

12) Y. Ikegami, unpublished data.

13) S. Imanishi and M. Ito, *J. Chem. Phys.*, **24**, 1272 (1956).

from the spectra indicated in Fig. 1. The comparatively broad absorption at 726 cm^{-1} in I is no longer visible in II and, therefore it can be assigned to the out-of-plane deformation vibration of C–O–H expected in this region. Analogous absorption bands have been recognized in carboxylic acids[7], chelated β-diketones[3] and hydroxyquinones[8]. This is also understandable since a broad absorption is seen in this region in tropolones in general but not in tropones[12]. The absorption at 767 cm^{-1} can be assigned to the C–H out-of-plane deformation vibration as the majority of 1, 2-disubstituted troponoids show strong absorption in this region[12] and because this absorption band has disappeared in deuterated tropolone (III), as shown in Fig. 5. Aside from such considerations in solution, the spectra in other states show a marked difference in shape, as shown in Fig. 4, and this fact indicates that such absorptions are easily affected by intermolecular action.

On Deuterated Tropolone. — Deuterated tropolone was obtained by heating a mixture of I and heavy water in a sealed tube at 150°C for a few hours. The compound III, obtained

TABLE II. OBSERVED FREQUENCIES (cm^{-1}) OF TROPOLONE

Infrared				Raman[d]	
Solid[a]	Liquid[a]	Solution[b,a]	Vapor[c]	In benzene	
3518 w	3450 vw	3450 vw			
			3245 sh		
		3151 m			O–H stretch.
3208 s	3195 s		3140 w		
		3120 m			
3049 vw	3060 vw	3051 sh	3055 w		C–H stretch.
3003 vw	3023 vw	3020 sh	3030 w		
1613 s	1614 vs	1618 vs	1628 vs	1610 (5)	C=O and
1548 vs	1553 s	1555 s	1573 s		C=C stretch.
1480 vs		1490 vs	1490 vs		C–O–H
	1476 vs				
1469 sh		1476 vs	1470 sh		C–C stretch.
		1444 s	1450 s	1418 (5)	
1425 vs	1426 vs				
		1425 sh	1425 sh		
1363 vw	1360 vw	1355 vw	1357 vw		2×675
		1317 sh			
1310 m	1300 m	1304 m	1305 s		
1266 vs	1264 vs	1267 vs	1265 vs	1262 (4)	C–O–H or
1238 vs	1245 vs	1251 vs	1250 sh		C–H in-plane deform.
1208 vs	1210 s	1213 m	1208 m	1208 (2)	
1049 m	1048 w	1048 vw			357+679[d]
1009 vw	990 vw	1000 vw			
958 m	956 m	953 m	940 m	959 (1)	
919 m	920 m	917 m	908 m		
874 w	871 m	873 w			2×436[d]
860 m	860 sh	854 w	860 w		
789 w					357+436
	769 s	767 m			
754 s			738 s	743 (3)	CH out-of-plane deform.
	740 s	726 s			C–C stretch.[d]
708 s			710 m		OH out-of-plane deform.
	711 s	713 s			
672 m	675 m	675 w	675 w	679 (2)	C–C–C ring deform.
531 vw					
433[e] m				436 (1)	C–C–C ring deform.
				357 (2)	C–C–C ring deform.

(vs: very strong, s: strong, m: medium, w: weak, vw: very weak, sh: shoulder)

a) The region of 3600~2600 cm^{-1} was measured by using CaF_2 prism; see Ref. 1.

b) Fig. 1a. c) Ref. 4. d) Ref. 5.

e) The region of 650~400 cm^{-1} was measured by using KBr prism only in solid (KBr disk).

by treating I twice with 99.78% heavy water for 5 hr., melted at 50°C, alone and in admixture with I. The ultraviolet spectrum of III is also very similar to that of I but their infrared spectra are very different. The absorption bands of III appeared at 3180, 1616, 1556, 1472, 1227 (in carbon tetrachloride) and 729 cm^{-1} (in carbon disulfide), all corresponding to those in Fig. 1a with similar shape. The absorption of C–H stretching vibration in I has become indistinct and appears as a weak band of C–D stretching vibration at 2266 cm^{-1} in III. Further, the strong absorptions at 1444, 1251 and 767 cm^{-1} in I have all disappeared and appear at around 1370, 1084 and 810 cm^{-1} in III (partly shown in Fig. 5), also indicating that these bands are closely related to the C–H bond in the seven-membered ring in I. However, there is not sufficient evidence to determine the position and number of deuteration.

Considerations Regarding Vibrational Spectrum of Tropolone.—The infrared absorption bands of tropolone, wave numbers of Raman lines reported by Imanishi[5], and their assignments are summarized in Table II. These assignments were chiefly based on the considerations of the foregoing deuteration and previously reported data[2-5]. Further, the weak absorptions at 1355 and 789 cm^{-1} were assumed to correspond respectively to the overtone, 2×675 cm^{-1}, and combination tone, $357+436$ cm^{-1}. The spectrum of tropylium cation[14], which has the most fundamental form among tropoids, was compared with that of tropolone and bands corresponding well were recognized in the lower wave number region. The vibration due to the seven-membered ring in the cation should not differ greatly from that of tropolone. It is expected to indicate similar wave numbers. Therefore, the absorptions at 675 and 433 cm^{-1} and Raman line at 357 cm^{-1} can be assigned to the ring deformation vibration. The few medium intensity bands observed clearly in the region of 1300～1200 cm^{-1}, which are characteristics of tropoids, may be assigned to the C–H deformation vibration of the seven-membered ring.

Experimental

Materials.—Recrystallization of tropolone (I), m. p. 50～51°C, was repeated several times from a mixed solvent of dioxane, dehydrated by metallic sodium, and 99.78% heavy water or from heavy water alone and 2-deuteroxytropone (II) was obtained as colorless needles, m. p. 51°C. Admixture of II and I showed no depression of the melting point. II easily reverted to I by the presence of a slight amount of moisture. Corresponding deuteroxyl compounds were also obtained by the same procedure from 3-bromotropolone, m. p. 108°C, and 3-methyltropolone, m. p. 50°C.

A mixture of 100 mg. of I and ca. 2 ml. of heavy water was heated in a sealed tube at 150°C for 5 hr. This procedure was repeated twice with fresh heavy water each time. The product purified by sublimation and recrystallization to colorless prisms (III), m. p. 50°C alone and in admixture with I.

U. V. $\lambda_{max}^{cyclohexane}$: 226, 239, 247 (sh.), 308 (sh.), 322, 355 and 374 mμ[15].

Infrared Absorption Spectra.—All infrared spectra were measured by a Perkin-Elmer model 21 infrared spectrophotometer equipped with a sodium chloride prism. The solid spectra were obtained by the potassium bromide disk method and solution spectra in carbon tetrachloride, purified several times by dehydration with phosphorus pentoxide, or carbon disulfide.

Summary

In order to find infrared absorption of tropolone, especially the absorption that can be assigned to the C–O–H group, the spectrum of 2-deuteroxytropone was measured and there were discussions chiefly on absorptions in the finger-print region. The absorption bands at around 3150, 1490, 1267 and 726 cm^{-1} were assigned to the vibration of C–O–H group. In this connection, some mention was made on deuterated tropolone and considerations were made on the assignment of vibrational spectra of tropolone, as summarized in Table II.

The author expresses his deep gratitude to Professor Susumu Kinumaki and Assistant Professor Koyo Aida, both of this institute, for their valuable guidance throughout the course of this work.

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14) K. Aida, *Sci. Repts. Research Inst. Tohoku Univ., Ser. A*, 8, 361 (1956); W. G. Fateley, B. Curnutte and E. R. Lippincott, *J. Chem. Phys.*, 26, 1471 (1957).
15) U. V. spectrum was measured by a Hitachi EPU-2A spectrophotometer.

The Dehydration Reactions by Means of Esters of Phosphoric Acid

By Teruaki MUKAIYAMA and Tsujiaki HATA

(Received July 9, 1960)

Dehydration reactions of primary nitroparaffins and aldoximes by means of organic reagents, such as isocyanates, carbodiimides, ketene acetals and vinylogs, have been described in preceding papers[1-3]. In the present study, dehydration reactions using esters of phosphoric acid have been investigated in order to extend the scope of dehydrating reagents.

In general, the dehydrating reagents can be classified in three classes according to their abilities of dehydration: The first class involves well known strong dehydrating reagents, such as sulfuric acid and phosphorus pentoxide, which remove the hydrogen atom and the oxygen atom at the ratio of 2:1 irrespective of the structures of the compounds to be dehydrated. The second class involves very weak dehydrating reagents, such as calcium chloride and sodium sulfate, which can not remove a water molecule other than that included in the form of water, such as the water of crystallization or adhering water. The third class involves organic dehydrating reagents, such as carboxylic acid anhydrides, carboxylic acid chlorides, isocyanates, carbodiimides and vinylogs, which show that moderate dehydrating abilities and selective intramolecular or intermolecular dehydration of organic compounds are affected with these reagents.

These three classes of dehydrating reagents can be modified by strengthening or weakening their respective dehydrating abilities. For example, it is possible to weaken the strong dehydrating ability of sulfuric acid or phosphorus pentoxide till it is moderate. Recently, it was reported[4] that polyphosphoric acid which is considered to be a mixture of hydrates of phosphorus pentoxide is a very useful dehydrating reagent under moderate conditions.

Esters of phosphoric acid used as dehydrating reagents in the present study are prepared by the reaction of phosphorus pentoxide with alcohols instead of phosphoric acid in the preparation of polyphosphoric acid:

$$n\ P_2O_5 + m\ ROH \rightarrow P{-}R\ (n{-}m),$$

where P—R (n—m) denotes an ester of phosphoric acid prepared by the reaction of n mol. of phosphorus pentoxide with m mol. of alcohol ROH. In general, the molar ratio of phosphorus pentoxide to monohydric alcohols is favorable when it is more than 1/3.

Esters of phosphoric acid are prepared very readily by adding alcohols to phosphorus pentoxide with vigorous agitation. In the preparation of these esters, it is desirable to make the reaction mixture as homogeneous as possible. For this purposes the addition of a pre-formed ester of phosphoric acid to phosphorus pentoxide in advance is favorable, just as shown in the preparation of polyphosphoric acid by the reaction of phosphorus pentoxide with phosphoric acid instead of water.

Monohydric alcohols, such as methyl, ethyl, *n*-propyl, isopropyl and *tert*-butyl alcohols, and also dihydric alcohol, and ethylene glycol, react with phosphorus pentoxide to give viscous esters of phosphoric acid, except in the case of *tert*-butyl alcohol. This does not form a homogeneous ester with phosphorus pentoxide, but the product separates into two layers, probably because of the branched structure of the alcohol. The esters of phosphoric acid thus formed, except that from *tert*-butyl alcohol, show nearly the same reactions. As an example of the dehydration reactions, the dehydrations using P—Et (2—5) prepared from 2 mol. of phosphorus pentoxide and 5 mol. of ethyl alcohol are described.

The reactions of benzaldoxime and heptanaldoxime with P—Et (2—5) give corresponding nitriles in quantitative yields without any accompanying side reactions:

$$RCH{=}NOH + P{-}Et\ (2{-}5) \rightarrow RC{\equiv}N$$

On the other hand, it was reported that the same dehydration reaction of an aldoxime could scarcely be observed with polyphosphoric acid and an acid amide formed by the Beckmann rearrangement of the aldoxime was mainly obtained because of the strong acid character of polyphosphoric acid. The yield of benzonitrile is maximum when benzaldoxime reacts with P—Et (2—5) for 15 min. and then it decreases with the time of heating as shown in Table I.

The dehydration of cyclohexanol to cyclohexene results by a simple treatment with

1) T. Mukaiyama and T. Hoshino, *J. Am. Chem. Soc.*, 82, 5339 (1960).
2) T. Mukaiyama and T. Hata, This Bulletin, 33, 1382 (1960).
3) T. Mukaiyama and T. Hata, ibid., 33, 1712 (1960).
4) F. D. Popp and W. E. McEwen, *Chem. Revs.*, 58, 321 (1958).

esters of phosphoric acid in a yield higher than when other dehydrating reagents, such as a catalytic amount of phosphoric acid, are used[5].

$$C_6H_{11}OH + P—Et\ (2—5) \rightarrow C_6H_{10}$$

The reaction of dibenzoylethane with P—Et (3—4) gives 2, 5-diphenylfuran in a nearly quantitative yield:

$$C_6H_5COCH_2CH_2COC_6H_5 + P—Et\ (3—4) \rightarrow$$

Similarly, the reaction of dibenzoylhydrazine with P—Et (2—5) gives 2, 5-diphenyl-1, 3, 4-oxadiazole in a good yield:

$$C_6H_5CONHNHCOC_6H_5 + P—Et\ (2—5) \rightarrow$$

The results of the dehydrations of benzaldoxime and cyclohexanol with the other esters are listed in Tables I and II. It should be noted that the reactivities of the five esters are nearly the same irrespective of their nature, except the ester of *tert*-butyl alcohol. It is also noted that the yield increases as the molar ratio of phosphorus pentoxide to alcohols increases and the maximum yield is obtained when benzaldoxime reacts with P—Et (3—4). P—Et (3—4), being a highly viscous liquid, is made to react more smoothly with benzaldoxime in a separate layer of a benzene solution.

Moreover, the esters of phosphoric acid possess several obvious advantages over polyphosphoric acid: 1) Since esters of phosphoric acid are less acidic than polyphosphoric acid, side reactions other than dehydration do not take place as shown in the dehydration of benzaldoxime. 2) In contrast to polyphosphoric acid, esters of phosphoric acid are soluble in organic solvents, such as chloroform, and reactions of organic compounds are conducted in homogeneous systems. 3) By the change of the molar ratio of phosphorus pentoxide to alcohols, the dehydrating ability of the esters is properly controlled.

The dehydrations by means of esters of phosphoric acid are considered to proceed through the bond fission of the pyrophosphate linkage by an attack of compounds containing a hydroxyl group to form 2 mol. of phosphates, and it is established that tetraethyl pyrophosphate reacts with benzaldoxime to give benzonitrile in a 76% yield along with 2 mol. of diethyl phosphate (95% yield).

$$(EtO)_2POOPO(OEt)_2 + C_6H_5CH{=}NOH \rightarrow 2(EtO)_2POOH + C_6H_5C{\equiv}N$$

Dehydrations of aldoximes, cyclohexanol, dibenzoylethane and dibenzoylhydrazine are well conducted with esters of phosphoric acid and also mostly with polyphosphoric acid, but dehydration of an acid amide with these reagents does not succeed and, when benzamide reacts with P—Et (2—5), ethyl benzoate is obtained in an 18% yield instead of the dehydrated product, benzonitrile, probably because of a replacement reaction of the alkoxyl group of the esters with the amino group of the acid amide.

$$C_6H_5CONH_2 + P—Et\ (2—5) \rightarrow C_6H_5COOEt$$

Since esters of phosphoric acid contain alkoxyl groups and form a carboxylic ester by the reaction with an acid amide, polyphosphonic acid is prepared from phosphorus pentoxide and benzenephosphonic acid.

$$C_6H_5PO(OH)_2 + P_2O_5 \rightarrow \text{polyphosphonic acid}$$

When benzamide reacts with the polyphosphonic acid, the dehydrated product, benzonitrile, is obtained, as expected, in a 60% yield.

Experimental

Preparation of Esters of Phosphoric Acid [P—R(*n*—*m*)].—To *n* mol. of phosphorus pentoxide was added *m* mol. of a monohydric alcohol or *m*/2 mol. of a dihydric alcohol dropwise with continuous stirring. When unchanged phosphorus pentoxide remained in a viscous ester, the whole was further heated on a boiling water bath until phosphorus pentoxide was completely dissolved. In general, the resulting esters, P—R (*n*—*m*), are viscous homogeneous liquids, but the ester from *tert*-butyl alcohol separated into two layers. P—Me (*n*—*m*)

TABLE I. THE REACTIONS OF α-BENZALDOXIME WITH VARIOUS ALKYL ESTERS OF PHOSPHORIC ACID, P—R (*n*—*m*), AT 100°C

P—R (*n*—*m*)	Reaction time, min.	Benzonitrile, yield %
P—Et (2—5)	5	60
	15	92
	60	70
	120	48
P—Et (1—3)	15	48
P—Et (2—5)	15	92
P—Et (1—2)	15	92
P—Et (3—4)	15	98
P—Me (2—5)	15	68
P—*n*Pr (2—5)	15	90
P—iso Pr (2—5)	15	92
P—*t*Bu (2—5)	15	53
P—EG (3—4)	15	87

5) L. F. Fieser, "Experiments in Organic Chemistry", D. C. Heath & Co., Boston (1955), p. 61.

and P—EG (*n*—*m*), prepared by the reactions of phosphorus pentoxide with methyl alcohol and ethylene glycol, respectively, were dark brown liquids, but they showed similar reactions to the other esters.

Reactions of α-Benzaldoxime with Esters of Phosphoric Acid.—A solution of α-benzaldoxime (5.0 g., 0.05 mol.) in 10 ml. dry benzene was added to 7.5 g. of P—Et (3—4) and the mixture was heated at 90°C with continuous stirring for 15 min. After removal of benzene, 4.2 g. (98% of the theoretical) of benzonitrile, b. p. 65~66°C (8 mmHg), was obtained. The results of the dehydration of α-benzaldoxime with P—R (*n*—*m*) are summarized in Table I.

Reaction of Heptanaldoxime with P—Et (3—4).—A solution of heptanaldoxime (2.6 g., 0.02 mol.) in 10 ml. dry benzene was added to 25 g. of P—Et (3—4). The mixture was heated on a boiling water bath for 30 min. with continuous stirring. After removal of benzene, 1.8 g. (80%) of heptanenitrile, b. p. 71~73°C (20 mmHg), was obtained.

Reactions of Cyclohexanol with Esters of Phosphoric Acid.—Cyclohexanol (6.0 g., 0.06 mol.) was added to 8.0 g. of P—Et (2—5) and the mixture was heated at 90°C with continuous stirring for 2 hr. 4.5 g., (92%) of cyclohexene, b. p. 47°C (200 mmHg), was obtained. The results of the dehydration of cyclohexanol with P—R (*n*—*m*) are summarized in Table II.

Reaction of Dibenzoylethane with P—Et (3—4).—Dibenzoylethane (1.0 g., 0.004 mol.) was added to P—Et (3—4) (5.0 g.) and the mixture was heated at 100°C with continuous stirring until the viscous mixture became brownish yellow in color. Then the mixture was poured into 150 ml. of ice water with vigorous stirring and the precipitate was collected by filtration. It was recrystallized from 95% ethanol and 0.86 g. (93%) of 2,5-diphenylfuran, m. p. 88~90°C, was obtained.

Reaction of Dibenzoylhydrazine with P—Et (3—4).—A solution of 1.0 g. (0.004 mol.) of dibenzoylhydrazine in 10 ml. dimethylformamide was added to 10 g. of P—Et (3—4). Then, the mixture was heated at 100°C for 2 hr. and poured into 200 ml. of ice water with vigorous stirring. The precipitate was collected by filtration and recrystallized from benzene to give 0.6 g. (65%) of 2,5-diphenyl-1,3,4-oxadiazole, m. p. 136°C.

Reaction of α-Benzaldoxime with Tetraethyl Pyrophosphate.—A mixture of tetraethyl pyrophosphate (2.9 g., 0.01 mol.) and α-benzaldoxime (1.21 g., 0.01 mol.) was heated at 95°C for 14 hr. and 0.78 g. (76%) of benzonitrile, b. p. 42~44°C (2 mmHg), and 2.92 g. (95%) of diethyl phosphate, b. p. 120~123°C (0.02 mmHg), were obtained.

Reaction of Benzamide with Polyphosphonic Acid.—To fused benzenephosphonic acid (2.0 g., 0.013 mol.) was added phosphorus pentoxide (3.0 g., 0.021 mol.) little by little with stirring during a period of 20 min. To the viscous polyphosphonic acid thus prepared was added benzamide (1.0 g., 0.008 mol.) with continuous stirring. After heating the mixture for 30 min. at 130°C, it was cooled at room temperature. Then it was dissolved in 20 ml. of water and extracted twice with 20 ml. of chloroform. The chloroform layers were combined and distilled under reduced pressure to give 0.5 g. (60%) of benzonitrile, b. p. 87~89°C (25 mmHg).

Table II. The reactions of cyclohexanol with various alkyl esters of phosphoric acid at 100°C

P—R (*n*—*m*)	Reaction time, hr.	Cyclohexene, yield, %
P—Et (2—5)	1.0	68
	1.5	92
	2.0	88
	3.0	93
P—Me (2—5)	2.0	88
P—*n*Pr (2—5)	2.0	99
P—iso Pr (2—5)	2.0	99
P—*t*Bu (2—5)	2.0	52

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Oxidizing Action of Hydroperoxides. V. On the Oxidation of Ketones

By Kazuhiro MARUYAMA

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In the previous paper of this series[1], it has been reported that hydroperoxides have a strong oxidizing action cooperating with alkali hydroxides. For example, alkylbenzenes are oxidized to the corresponding alcohols, ketones and carboxylic acids. Further, alkyl aryl ketones are split very smoothly to benzoic acid derivatives and alcohols,—but diaryl ketones are not cleft by these oxidizing agents[2]. Furthermore, in order to obtain more extensive knowledge of the reaction, the same kinds of reactions were examined on some ketones; isopropyl phenyl ketone, cyclohexyl phenyl ketone *p*-chloroacetophenone, desoxybenzoin, phenyl *p*-chlorobenzyl ketone, benzoin, benzil, α-tetralon, 3-pentanone, 3-heptanone and cyclohexanone were examined. All these reactions were performed in nonaqueous solvent and the examined ketones were also cleft smoothly with the one exception of cyclohexanone. An outstanding difference between this cleavage reaction mechanism and the Baeyer-Villiger mechanism is that any C–C linkage between carbonyl carbon and aromatic carbon in alkyl aryl ketones, is never attacked.

Experimental

Reagents.—The reagents cited in Table I were synthesized by the Friedel-Crafts reaction.

Benzoin was prepared by condensation of benzaldehyde, m. p. 137°C; semicarbazone, m. p. 206°C. Benzil was prepared by nitric acid oxidation of benzoin, m. p. 95°C. α-Tetralon was synthesized from tetralin after Thompson's method, checked by Shriner and Poland[3], b. p. 107°C/2 mmHg, n_D^{15}, 1.5640; semicarbazone, m. p. 217°C. 3-Pentanone and 3-heptanone, the commercially available guaranteed grade reagent was used without further purification. *tert*-Butylhydroperoxide was snythesized by the action of 30% hydrogen peroxide on *tert*-butanol according to Milas and Surgenor's method[4] and purified by fractional distillation under reduced pressure. B. p. 36°C/19 mmHg, n_D^{27}: 1.3967. Cyclohexanone, the commercially available guaranteed grade reagent was treated with potassium permanganate and was purified by distillation. b. p. 157°C, Semicarbazone, m. p. 155°C.

Reaction Procedure.—The reaction apparatus and the treatments of reaction mixture are quite the same as that described in the previous paper[2]. With the exception of the case with benzil and α-tetralon the experiment was conducted as following.

The weighed ketone was dissolved in purified monochlorobenzene (150 cc.). Carbonate free powdered potassium hydroxide was added to the mixture after the air in the reaction vessel was completely exchanged with dry pure nitrogen. As soon as the temperature of the reaction mixture reached 70°C, *tert*-butylhydroperoxide was added. The temperature raising of about 10°C was observed. After six hours, the reaction mixture was extracted with 100 g. of water three times. The water extract was acidified with 2 N-sulphric acid and the precipitated benzoic acid derivative was collected and weighed. The filtrate was neutralized with conc. ammonia

TABLE I

Ketones	(B. p.) or [m. p.] °C	n_D^{15}	Semicarbazones m. p., °C	Oxime m. p., °C	Synthesized from
Isopropyl phenyl	(95/10 mmHg)	1.5196	181		benzene and isobutyl chloride
Cyclohexyl phenyl	[59~60]		175		benzene and cyclohexyl chloride
p-Chloroaceto-phenone	(99/7 mmHg) [19~20]		148		chlorobenzene and acetyl chloride
Desoxybenzoin	(177/12 mmHg) [60]		148		benzene and phenyl acetyl chloride
Phenyl *p*-chlorobenzyl	[138]			95~96	benzene and *p*-chlorophenylacetyl chloride

1) K. Maruyama, R. Goto and H. Suzuki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 521 (1959).
2) This Bulletin, **33**, 1516 (1960).
3) Organic Syntheses, **20**, 94 (1940).
4) N. A. Milas and D. Sürgenor, *J. Am. Chem. Soc.*, **68**, 205, 643 (1946).

Table II. Oxidation of ketones with *tert*-butylhydroperoxide
(Temp. 60°C, 6 hr.)

Ketone	Hydroperoxide g. (mol.)	Ketone recovered	Reaction product
1. Isopropyl phenyl ketone 10.0 g.	*tert*-Butylhydroperoxide 2.0 g.	8.5 g.	Benzoic acid 1.05 g., isopropanol (*tert*-butanol, methanol)
2. Cyclohexyl phenyl ketone 10.0 g.	*tert*-Butylhydroperoxide 2.0 g.	9.0 g.	Benzoic acid 0.30 g., adipic acid, non-identified acid (*tert*-butanol, methanol)
3. *p*-Chloroaceto-phenone 10.0 g.	*tert*-Butylhydroperoxide 2.0 g.	7.0 g.	*p*-Chlorobenzoic acid 1.2 g. (*tert*-butanol, methanol)
4. Desoxybenzoin 10.0 g.	*tert*-Butylhydroperoxide 2.0 g.	8.3 g.	Benzoic acid 1.50 g. (*tert*-butanol, methanol)
5. Phenyl *p*-chloro-benzyl ketone 10.0 g.	*tert*-Butylhydroperoxide 2.0 g.	8.0 g.	Benzoic acid 0.30 g., *p*-chlorobenzoic acid 0.40 g. (*tert*-butanol, methanol)
6. Benzoin* 10.0 g.	*tert*-Butylhydroperoxide 2.0 g.	8.0 g.	Benzoic acid 1.9 g. (*tert*-butanol, methanol)
7. Benzil** 10.0 g.	*tert*-Butylhydroperoxide 2.0 g.	8.0 g.	Benzoic acid 1.8 g., benzilic acid (trace) (*tert*-butanol, methanol)
8. α-Tetralon*** 8.2 g.	*tert*-Butylhydroperoxide 2.0 g.	—	*O*-Carboxyhydrocinnamic acid 0.43 g., *O*-carboxycinnamic acid 0.07 g., phthalonic acid 0.01 g., resin.
9. 3-Pentanone 8.6 g. (0.1 mol.)	*tert*-Butylhydroperoxide 5.4 g. (0.06 mol.)	—	Propionic acid (main), acetic acid } total acid 0.02 mol.
10. 3-Heptanone 11.4 g. (0.1 mol.)	*tert*-Butylhydroperoxide 5.4 g. (0.06 mol.)	—	*n*-Valeric acid (main), propionic acid, *n*-butyric acid, acetic acid } total acid 0.016 mol.
11. Cyclohexanone 9.8 g. (0.1 mol.)	*tert*-Butylhydroperoxide 5.4 g. (0.06 mol.)	almost completely recovered	No reaction (oxygen, *tert*-butanol, methanol)

* In this case, the solution of benzoin suspended with potassium hydroxide was deeply colored violet before the addition of hydroperoxide. As the peroxide was dropped, however, the violet color disappeared.

** In this reaction, potassium hydroxide was added in the mixture of benzil and hydroperoxide in order to avoid the so-called "benzilic acid rearrangement." By this precaution, the rearrangement was in practice avoided.

*** In this case, benzene was used as a solvent and its solution of α-tetralon and hydroperoxide were dropped to suspension of potassium hydroxide in benzene. However, a large quantity of resinous product was not avoided.

and was concentrated to 10 cc. and subjected to a paper chromatographic analysis.

The obtained experimental results are shown in Table II.

Benzoic Acid.—In the reaction 1, 2, 4, 5, 6 and 7 benzoic acid was obtained by the acidifying of the water extraction of the reaction mixture. The crude products were recrystallized from the water-alcohol mixture. The acid was identified by the mixed melting point method and paper chromatography.

Isopropanol.—In reaction 1, isopropanol was collected in a trap cooled by ice-salt mixture. This was identified as its phenylurethan derivative (from ligroin m. p. 88°C) and also verified by gas chromatography.

Found: C, 66.98; H, 7.22. Calcd. for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31%.

Adipic Acid.—In reaction 2, the acid was found in the solid acid of reaction products and in the concentrated part of the filtrate. Adipic acid was identified by paper chromatography (R_f 0.22, solvent: 5% ammonia 1 vol.+isopropanol 4 vol., temp. 15~20°C). Another acid (R_f 0.44) was found on the paper chromatogram accompanying benzoic acid and adipic acid. But, this acid could not be identified.

***p*-Chlorobenzoic Acid.**—In reaction 3, acid was obtained by the acidifying of the water extract of the reaction mixture, and was identified as *p*-chlorobenzoic acid by the mixed melting point method and paper chromatography (m. p. 243°C).

Found: C, 53.77; H, 3.11. Calcd for $C_7H_5O_2Cl$: C, 53.69; H, 3.21%.

In reaction 5, *p*-chlorobenzoic acid was obtained by the acidifing of the water extract of the reaction mixture accompanying benzoic acid, and was easily separated from benzoic acid by crystallization from hot water. The obtained crude acid was recrystallized from the water-alcohol mixture, m. p. 242~243°C and was identified by the mixed melting point method and paper chromatography.

Benzilic Acid.—In reaction 7, a trace of benzilic acid was found in the acid products, and was detected paperchromatographically and identified by comparison with a known sample.

***o*-Carboxyhydrocinnamic Acid.**—In reaction 8, the acid was obtained as the main reaction product. The water extract of the reaction mixture was acidified and the obtained precipitation was recrystallized from hot water. *o*-Carboxyhydrocinnamic acid is slightly soluble in hot water and separated from insoluble acid. Repeated recrystallization resulted in the paperchromatographically pure product, and was identified by the mixed melting point method and paper chromatography (R_f 0.21 solvent: 5% ammonia 1 vol. isopropanol 4 Vol., room temp.) m. p. 166~167°C.

Found: C, 62.14; H, 5.30. Calcd. for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19%.

***o*-Carboxycinnamic Acid.**—In reaction 8, this acid was obtained as a product insoluble in hot water, but soluble in hot alcohol, m. p. 173~174°C and was identified by the mixed melting point method and paper chromatography.

Phthalonic Acid.—In reaction 8, phthalonic acid was obtained as the benzene soluble part of acid products, m. p. 150~151°C and was identified by the mixed melting point method and on a paper chromatogram by comparison with a known sample.

Methanol and *tert*-Butanol.—These products were collected in a trap cooled by ice-salt, and analyzed gaschromatographically. *tert*-Butanol was separated as its phenylurethan, m. p. 136°C.

Found: C, 68.86; H, 7.93. Calcd. for $C_{11}H_{15}NO_2$: C, 68.40; H, 7.80%.

***n*-Valeric Acid, *n*-Butyric Acid, Propionic Acid and Acetic Acid.**—These acids were detected by paper chromatography and their total acid contents were determined by titration.

Discussion

It was discussed in the previous paper[1], almost all of the examined ketones, there being only one exception, are subjected to a cleavage reaction by *tert*-butylhydroperoxide. These reactions are summarized in the next equations.

i) Aromatic ketone

$$\mathrm{Ar\text{-}CO\text{-}R} \xrightarrow[\mathrm{KOH}]{t\text{-}\mathrm{BuOOH}} \mathrm{ArCOOH} + \mathrm{ROH} \qquad (1)$$

R=alkyl

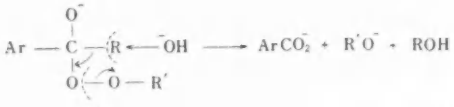
ii) Aromatic α, β-diketone

$$\mathrm{ArCO\cdot COAr'} \xrightarrow[\mathrm{KOH}]{t\text{-}\mathrm{BuOOH}} \mathrm{ArCOOH} + \mathrm{Ar'COOH} \qquad (2)$$

iii) Aliphatic ketone

$$\mathrm{RCOR'} \longrightarrow \begin{cases} \mathrm{RCOOH} + \mathrm{R'OH} \\ \mathrm{R'COOH} + \mathrm{ROH} \end{cases} \qquad (3)$$

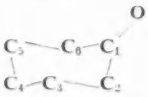
From results of Table II, it could be confirmed that in general, an alkyl aryl ketone can be cleft to benzoic acid derivative and alcohol by hydroperoxide cooperating with alkali hydroxide. The hydroperoxide was reduced to alcohol — e. g. *tert*-butylhydroperoxide → *tert*-butanol. Furthermore, aromatic α, β-diketone was also cleft by the same oxidizing reagent to benzoic acid derivatives. It was a outstanding difference from the cleavage of aromatic ketones by peracids according to Baeyer-Villiger reaction that phenolic product was not found in the oxidation products. This difference, of course, is ascribed to the different reaction mechanism, for this kind of reactions are performed in alkaline medium. As it was briefly discussed in the previous paper, the reason of the absence of phenolic product may be due to a difficulty of formation of phenyl cation (or of S_N2-type reaction at nucleus carbon) at the moment of scission from the complex [I], which is consisted of ketone and hydroperoxide.



[I] (4)

The same kind of cleavage reaction occurred even in the aliphatic ketones, but in this case, the two linkages on both sides of carbonyl carbon have a chance of scission. The chance of scission, however is determined by the stability of the alkyl group as a cation*.

For cyclohexanone, which is only one exception to the cleavage reaction, it may be guessed that the complex can not be formed. This is because, in the alkaline medium the attack of the hydroperoxide anion to the positively polarized carbonyl carbon atom will be most easily performed on the opposite side of the negatively polarized oxygen atom and the steric hindrance which will be caused by the axial hydrogens on C_2, C_6, C_3 and C_5 and by the C_3, C_4 and C_5 carbon atom, against the attack of the hydroperoxide anion makes the formation of complex [I] impossible.



The author is indebted to Professor Ryozo Goto for discussion and encouragement throughout this investigation.

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* This was confirmed in the case of methyl ethyl ketone and of methyl isopropyl ketone in the homogeneous system (O. Soga, K. Maruyama and R. Goto, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 668 (1960).

Oxidizing Action of Hydroperoxides. VI. On the Oxidation of Ketones

By Kazuhiro MARUYAMA

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In the previous work[1], it was reported that hydroperoxides acted as a strong oxidizing agent in the presence of alkali hydroxide, and especially a vigorous reaction occurred with alkyl aryl ketone and resulted in a cleavage of C–C linkage between the carbonyl carbon and the alkyl carbon. The mechanism of this reaction must be different from the "Baeyer-Villiger" mechanism, because alkyl aryl ketone does not produce any phenolic products and diaryl ketone affords none of its reaction products.

From this point of view, the following three points were examined:

i) In the first place, it must be decided that the cleavage reaction of ketone with hydroperoxide can proceed by way of an intermediate complex, in which the hydroperoxide anion will be added to the carbonyl carbon atom of the ketone. And, if not, an active oxygen atom isolated from the hydroperoxide anion will be responsible for the cleavage reaction. In order to examine these points, a method of competitive reaction was employed; that is, with the selection of acetophenone-1-^{14}C (carbonyl ^{14}C) as a standard ketone, the reactivity among methyl derivatives of acetophenone, substituted on the methyl group, was compared.

ii) The influence of *p*-substituent to acetophenone towards the reactivity was confirmed.

iii) The progression of cleavage reaction was traced for some ketones — acetophenone, ethyl phenyl ketone and isopropyl phenyl ketone.

Experimental

Reagent. — Ketones used as reagents are all synthesized, as can be seen from the following tabulation.

Acetophenone-1-^{14}C was prepared from benzene and acetyl-1-^{14}C chloride. Acetyl-1-^{14}C chloride was synthesized from sodium acetate-1-^{14}C according to Anker's method.[2] The obtained acetophenone-1-^{14}C has b. p. 196~199°C (yield 75%). *tert*-Butyl-hydroperoxide was prepared from *tert*-butanol and

TABLE I

Ketones	(B. p.), [m. p.] °C	Semicarbazone m. p. °C	Oxime m. p. °C	2,4-Dinitrophenylhydrazone m. p.	Synthesized from
Ethyl phenyl	(105/20 mmHg), [21]				benzene and propionyl chloride
p-Chlorobenzyl phenyl	[138]		95~96		benzene and *p*-chlorophenylacetyl chloride
Isopropyl phenyl	[59~60]	175			benzene and isobutyloyl chloride
tert-Butyl phenyl	(220~222) (104~106/17 mmHg)			166~168	isopropyl phenyl ketone and methyl iodide (Halle's method)*
p-Methylacetophenone	(222)	205			toluene and acetyl chloride
p-Methoxyacetophenone	(138/14 mmHg) [38~39]	195			anisole and acetyl chloride
p-Phenylacetophenone	[120~121]		184~185		biphenyl and acetyl chloride
p-Chloroacetophenone	(99/7 mmHg), [20]	202~204			chlorobenzene and acetyl chloride
p-Bromoacetophenone	(130~131/12 mmHg) (51]				bromobenzene and acetyl chloride

* M. A. Halle and E. Bauer, *Compt. rend.*, **148**, 72 (1909).

1) K. Maruyama, This Bulletin, **33**, 1516 (1960).

2) H. S. Anker, *J. Biol. Chem.*, **176**, 1333 (1948).

30% hydrogen peroxide according to Milas's method[3], b. p. 36 °C/19 mmHg, n_D^{25} 1.3967.

Reaction Procedure. — *1) Competitive Reaction with Acetophenone-1-^{14}C.*—A three-necked 200cc. flask, equipped with a thermometer, a dropping funnel and a reflux condenser was placed in a thermostat, controlled to (70±1 °C). A mixture of 0.01 mol. of acetophenone-1-^{14}C and 0.01 mol. of testing ketone, dissolved together in 50 g. of monochlorobenzene, was charged in the flask and the contents were agitated vigorously with a magnetic stirrer. When the temperature of the contents became constant, 0.062 mol. of finely powdered pure potassium hydroxide* was added and 0.06 mol. of *tert*-butylhydroperoxide, dissolved in 10 g. of monochlorobenzene, was dropped through a dropping funnel within three minutes. After one hour, the reaction was finished. The contents were cooled with ice, added with 50 cc. of ether and extracted with 20 cc. of water three times. The water extract was collected and acidified with 6N hydrochloric acid, and then precipitated benzoic acid was collected and purified. A hundred milligrams of the obtained benzoic acid was used for the counting** of the activity in each reaction.

2) Comparison of Reactivity of p-Substituted Acetophenone.—The same reaction apparatus as that described above was employed. A mixture of 0.02 mol. of ketone, 0.062 mol. of finely powdered pure potassium hydroxide dissolved in 50 g. of monochlorobenzene and a solution of 0.06 mol. of *tert*-butylhydroperoxide dissolved in 10 g. of monochlorobenzene was caused to react in the reaction vessel. After one hour, the reaction was ceased, the mixture was immediately cooled with ice, added with 50 cc. of ether, and extracted three times with 20 cc. of water each. The water extract was acidified with 14 cc. of 6N hydrochloric acid and extracted three times with 20 cc. of ether each. The ether extract was washed with 5 cc. of water three times, and then the ether extract was added with pure ethanol till the total volume became just 100 cc., and titrated with 0.054 N sodium hydroxide solution. Thus the obtained benzoic acid was determined.

3) Measurement of Progression of Cleavage Reaction.—In these reactions, 0.042 mol. of ketone, 0.056 mol. of *tert*-butylhydroperoxide and 0.056 mol. of finely powdered pure potassium hydroxide were used and reaction procedures were the same as in 2. The reaction mixture was not completely homogeneous, hence a pipetting-out method could not be used, and so the total reaction mixture was used for analysis after the definite time of reaction had elapsed. Therefore, to determine the cleavage velocity of a ketone, five reactions under the same conditions should be performed. In this method, the accuracy of the measurements was fairly good (see Fig. 2).

Results and Discussion

Competitive Reaction with Acetophenone-1-^{14}C. —The results are given in Table II. A relative reactivity derived from counting the amount of the benzoic acid obtained in each reaction is cited in column 4.

TABLE II. COMPETITIVE REACTION WITH ACETOPHENONE-1-^{14}C

	Ketone	Counting number*) (c. p. m.)	Reactivity
1.	$C_6H_5\cdot C(=O)\cdot CH_3$	1000±19	1
2.	$C_6H_5\cdot C(=O)\cdot CH_2CH_3$	514±15	2.9
3.	$C_6H_5\cdot C(=O)\cdot CH_2C_6H_4Cl(p)$	860±19	1.3
4.	$C_6H_5\cdot C(=O)\cdot CH(CH_3)_2$	707±19	1.8
5.	$C_6H_5\cdot C(=O)\cdot CH$(bicyclo[2.2.2]octane)	1706±27	0.2
6.	$C_6H_5\cdot C(=O)\cdot C(CH_3)_3$	1111±19	0.8

*) A hundred milligrams of the obtained benzoic acid was used for the counting of the activity in every reaction.

Conditions of reactions: Temp. 70°C, reaction time 1 hr.

(acetophenone-1-^{14}C 0.01 mol. + ketone 0.01 mol. + *tert*-butyl hydroperoxide 0.06 mol. + powdered potassium hydroxide 0.062 mol.) dissolved in 60 g. of monochlorobenzene.

3) N. A. Milas and D. Sürgenor, *J. Am. Chem. Soc.*, **68**, 205, 643 (1946).

* After potassium hydroxide was added, the contents were slightly colored in brown, but soon decolorizeb when hydroperoxide was added.

** A G-M counter was applied.

TABLE III. COMPARISON OF REACTIVITY OF *p*-SUBSTITUTED ACETOPHENONE

	Ketone	Substituent	Titration neeeded volume of 0.054 N-NaOH soln. (V)
1.	$C_6H_5\cdot C(=O)\cdot CH_3$	-H	63.3
2.	$p\text{-}CH_3\cdot C_6H_4\cdot C(=O)\cdot CH_3$	$-CH_3$	34.0
3.	$p\text{-}CH_3O\cdot C_6H_4\cdot C(=O)\cdot CH_3$	$-OCH_3$	33.8
4.	$p\text{-}C_6H_5\cdot C_6H_4\cdot C(=O)\cdot CH_3$	$-C_6H_5$	65.0
5.	$p\text{-}Cl\cdot C_6H_4\cdot C(=O)\cdot CH_3$	-Cl	170.5
6.	$p\text{-}Br\cdot C_6H_4\cdot C(=O)\cdot CH_3$	-Br	212.4

Conditions of reactions: Temp. 70°C, reaction time 1 hr.
{ketone 0.02 mol., *tert*-butylhydroperoxide 0.06 mol., powdered potassium hydroxide 0.062 mol.} dissolved in 60 g. of monochlorobenzene.

From the above results, it may be seen that the successive methyl substitution on the methyl group of acetophenone produces a ketone which has the maximum reactivity upon *tert*-butylhydroperoxide in the series of acetophenone derivatives; that is, the relative reactivities of acetophenone, ethyl phenyl ketone, isopropyl phenyl ketone and *tert*-butyl phenyl ketone were about 1:3:2:1. On the other hand, the reactivity of *p*-chlorobenzyl phenyl ketone is one third of that of ethyl phenyl ketone. The same result is also seen in the comparison between isopropyl phenyl ketone and cyclohexyl phenyl ketone. The latter is about one tenth of the former in its reactivity. Moreover, *tert*-butyl phenyl ketone is even more reactive upon *tert*-butylhydroperoxide than cyclohexyl phenyl ketone is.

These results obtained above would lead to the conclusion that the steric effect of the alkyl group and the effect of the stability of the alkyl group as its cation are conversely responsible for the reactivity of alkyl phenyl ketone, that is, the size of the alkyl group obviously increases in the following order, $CH_3 < CH_2CH_3 < CH(CH_3)_2 < C(CH_3)_3$ and so the more bulky the alkyl group is, the larger is the steric hindrance of alkyl groups against the attack of *tert*-butylhydroperoxide on the carbonyl group (F-strain). On the other hand, the stability of the alkyl group as a cation is in the following order $CH_3 < CH_2CH_3 < CH(CH_3)_2 < C(CH_3)_3$. If the alkyl group of an alkyl aryl ketone is cleft as a cation*, the same order of the relative reactivity may be expected. Then, based on these considerations, it seems reasonable to suppose that the appearance of maximum reactivity in ethyl phenyl ketone depends upon the overlap of the conversely acting two effects.

Comparison of Reactivity of *p*-Substituted Acetophenones.—Relative reactivities of *p*-substituted acetophenones are given in Table III and their relation to Hammett's σ_p value is shown in Fig. 1. From the results obtained, it can be deduced that the more electron attractive the substituent of an acetophenone, the

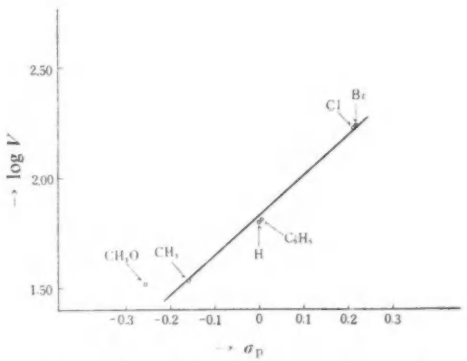


Fig. 1. The relation between σ_p value and reactivity of *p*-substituted acetophenones.

* This is also supported from the following facts: i) alcohol derived from the alkyl group was confirmed as a reaction product and ii) diaryl ketones could not be cleft by these reagents.

more reactive is the acetophenone derivative. Furthermore, Hammett's plot of $\log V$ to σ_p gives straight line (see Fig. 1). It may be deduced that, in general, an electron attractive substituent on the phenyl group raises the reactivity of acetophenone derivatives for *tert*-butylhydroperoxide.

Measurement of Progression of Cleavage.—In order to study the progression of reaction and to elucidate its mechanism, the cleavage reaction of acetophenone, ethyl phenyl ketone and isopropyl phenyl ketone was examined. From the results obtained, the following may be written (see Fig. 2).

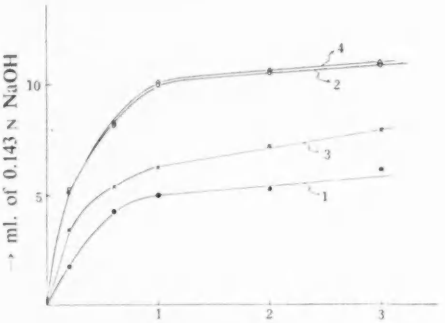


Fig. 2. Progression curve of reaction derived from titration curve of produced benzoic acid.

(1) $C_6H_5COCH_3$ 0.042 mol.
(2) $C_6H_5COC_2H_5$ 0.042 mol.
(3) $C_6H_5COCH\begin{matrix}CH_3\\CH_3\end{matrix}$ 0.042 mol.
(4) $\begin{matrix}C_6H_5COC_2H_5\\As_2O_3\end{matrix}$ 0.042 mol. 0.0005 mol.

Conditions of reactions: Temp. 70°C
(ketone 0.042 mol.)
tert-butylhydroperoxide 0.056 mol.
(powdered potassium hydroxide 0.056 mol.)
dissolved in 60 g. of monochlorobenzene.

i) There is no induction period for any reaction.

ii) The addition of arsenious acid to the reaction mixture has no effect.

iii) The reproducibility of these reactions is fairly good.

From the above three points, it might be possible to obtain the conclusion that the cleavage of ketones with hydroperoxides in the presence of alkali hydroxide is not a chain reaction.

Reaction Mechanism.—On the examination of reaction mechanism, the followings should be born in mind:

i) Alkyl aryl ketone is cleft with hydroperoxide cooperating with alkali hydroxide and produces benzoic acid derivative and alcohol derived from the alkyl group of ketone.

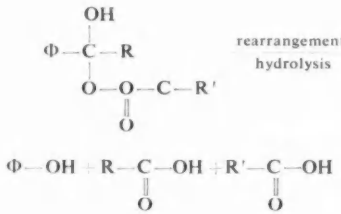
ii) Diaryl ketone (e.g. benzophenone, *p*-nitrobenzophenone and fluorenone) can not be cleft with this oxidizing reagent.

iii) In the series of methyl substituted derivatives of acetophenone having the substituent on the methyl group, a maximum reactivity is observed in ethyl phenyl ketone.

iv) In *p*-substituted derivatives of acetophenone, the more electron attractive the *p*-substituent is, the larger is the reactivity upon hydroperoxide.

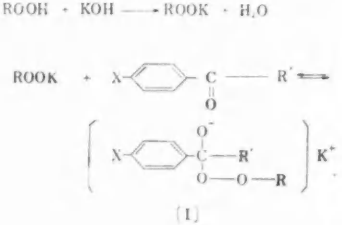
v) These reactions have no induction period, and arsenious acid which is known as an inhibitor of the chain reaction has no effect.

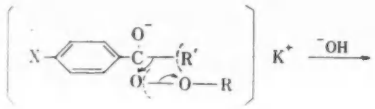
In view of i)—iii), this cleavage reaction of ketone should be different from the "Baeyer-Villiger" reaction, which is a cleavage reaction of ketone by peracid, for the cleavage of ketone according to "Baeyer-Villiger" mechanism is of a rearrangement of carbanion to oxygen cation.

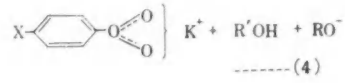


If this reaction, which is an oxidizing action of hydroperoxide cooperating with alkali hydroxide upon ketone, is supposed to follow the same mechanism as that of B. V., phenolic derivative and fatty acid must be produced, but, in fact, only benzoic acid derivative and fatty alcohol are obtained and so the C–C linkage between carbonyl carbon and phenyl carbon is not cleft. In order to explain these results conveniently, the following reaction mechanism seems very probable.

This mechanism implies that the hydroperoxide, first produces its potassium salt, and then this salt attacks carbonyl carbon and gives a complex(I), which is cleft by hydroxide anion to acid and alcohol. Reaction 3 should be a reversible reaction and the position of equilibrium would probably be settled under



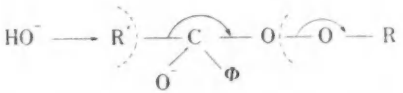




-------(4)

$$RO^- + H_2O \longrightarrow ROH + {}^-OH \quad \text{-------(5)}$$

the influence of the size of alkyl group. F-Strain of alkyl group against the attack of hydroperoxide anion on the carbonyl carbon may act as a factor inhibiting the formation of complex [I]. On the other hand, the back-side attack of hydroxide anion on the alkyl group may play an important role* (Eq. 4) for the cleavage of complex I. The same equilibrium as in Eq. 3 may exist in the case of diaryl ketone, but the succeeding back-side attack of hydroxide anion would not act effectively, so that diaryl ketones could not be cleft. However, the cleavage reaction may be started by the scission of R′-cation from complex I, and a promoting action of HO^- anion for this, too, may act and at the same time the scission of RO^- anion may take place concertedly with the above process, that is:



As the result of this cleavage reaction, benzoic acid derivatives, R′OH and ROH are produced. According to this mechanism, it is quite possible that a maximum reactivity observed in ethyl phenyl ketone (discussion 3) is caused by a result of two counter-acting effects which are effects of R′ cation and steric hindrance for the back-side attack of HO^- anion. Moreover, the increase of of F-strain, caused by the increase in size of the alkyl group, for the formation of complex I (Eq. 3) may contribute to the decrease of reactivity. On the other hand, the promoting action of an electron attracting substituent on the phenyl group can be explained as follows; that is, the increase of stability of the *p*-substituted benzoate anion by an electron attracting substituent may cause an increase of driving force for the cleavage reaction of the complex [I].

Contrary to the above mechanism, i) the possibility of contribution of radicals for the cleavage reaction of the complex [I], ii) the possibility of contribution of enol-type of ketone this cleavage reaction, and iii) the possibility of contribution of atomic oxygen isolated completely from ROO^- may be doubted. However, i) diaryl ketones can not be cleft and phenolic derivatives are not produced in any cleavage reaction, ii) *tert*-butyl phenyl ketone is cleft almost easily as acetophenone, and iii) when formaldehyde, acetaldehyde, propionaldehyde, acetone and methyl ethyl ketone are selected as carbonyl compounds, the decomposition velocity of hydroperoxide is strikingly different according to the structure of carbonyl compounds[5]. For example, *tert*-butylhydroperoxide did not decompose in the reaction with acetone (at 30°C), but the same hydroperoxide was decomposed in the reaction with methyl ethyl ketone under the same condition. If the isolated oxygen atom acts as an oxidizing agent, there must be no such phenomena.

The author is indebted to Professor Ryozo Goto for discussion and encouragement throughout this investigation.

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* In fact, it was confirmed that an increase of hydroxide anion, in homogeneous alkaline solution, accelerates the cleavage of the complex, which is inferred from the decomposition velocity of hydroperoxide, in the case of methyl ethyl ketone. The decomposition velocity of hydroperoxide was studied on the next two reaction mixtures;

A: methyl ethyl ketone 0.05 mol., *tert*-butylhydroperoxide 0.028 mol. and potassium hydroxide 0.03 mol. are all dissolved in 250 ml. of water.

B: methyl ethyl ketone 0.05 mol., *tert*-butylhydroperoxide 0.028 mol. and potassium hydroxide 0.06 mol. are all dissolved in 250 ml. of water.

The decomposition velocity of the hydroperoxide was in A: 0.30 mol./l hr., in B: 0.40 mol./l hr. at 35.0°C and in A: 0.49 mol./l hr., in B: 0.60 mol./l hr. at 40.2°C (unpublished work).

Cf. Maruyama, Goto and Kitamura, Oxidizing Action of Hydroperoxide III. under the contribution to *J. Chem. Soc. Japan, Pure Chem. Soc.* (*Nippon Kagaku Zasshi*).

5) O. Soga, K. Maruyama and R. Goto, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **81**, 668 (1960).

Rates of Solvolysis of Di-p-toluenesulfoxycyclohexanes

By Nobuo Mori

(Received May 23, 1960)

In the previous paper[1] it was reported that *trans*-1,3-di-*p*-toluenesulfoxycyclohexane, in which one of two toluenesulfoxyl groups was axial and the other equatorial in stable form, was solvolyzed more rapidly than the cis form, in which two toluenesulfoxyl groups were equatorial in stable form, in agreement with the general rule as described below. However, it was unexpectedly observed that solvolysis of *trans*-4-hydroxy- or -acetoxy-cyclohexyl *p*-tosylate in which two substituents were equatorial proceeded at a rate twice as fast as that of the corresponding cis isomer in which one of two substituents was axial and the other equatorial[2]. In connection with the unexpected result mentioned above it was desirable to study further the configuration and the reactivity of the 4-substituted cyclohexyl *p*-tosylates.

In the present work, also in relation to the problem mentioned above, the solvolysis of 1,2- and 1,4-di-*p*-toluenesulfoxycyclohexanes (described as ditosylates in this paper) has been made.

Experimental

Samples.—*cis*- and *trans*-Cyclohexane-1,2- and -1,4-diols used as starting materials were those which were previously prepared[2,3]. Each of them was treated in pyridine at 0 to 5 °C with two equivalent quantities of *p*-toluenesulfonyl chloride according to the conventional method, and the resulting ditosylate was recrystallized from a mixture of benzene and ligroin. The ditosylates obtained in this way had respectively the following melting points.

Position of tosyl groups	M. p. (reported m. p.), °C
cis-1,2	129～130 (128.5～129.5[4])
trans-1,2	109～110 (109[4])
cis-1,4	98～98.5 (98～99[5])
trans-1,4	159 (159[5])

Procedure for Rate Measurements.—Solvolysis rates were measured at 99.8 °C in ethanol (98.5% by weight), in methanol (99.5% by weight) and in acetic acid containing a slight excess of acetic anhydride, by the usual ampoule technique[1,2]. Concentrations (all given at room temperature) of ditosylates were in the range from 0.005 to 0.01 mol./l., since they are less soluble in these solvents, especially in alcohol. Solvolysis of 1,4-ditosylates was performed in 0.01 mol./l. in acetic acid and also in 0.005 mol./l. in methanol since the solubility of the compounds in ethanol was very small, and that of 1,2-ditosylates was performed in ethanol. The reactions were followed by titrating at intervals for the sulfonic acid liberated or the alkali consumed during the solvolysis. Titrations in acetic acid were carried out with a 0.05 N solution of anhydrous sodium acetate or *p*-toluenesulfonic acid in acetic acid using bromophenol blue as indicator. In methanol and ethanol, a 0.05 N aqueous solution of sodium hydroxide or hydrogen chloride was used as a standard solution for titration with phenolphthalein as indicator. Rate constants were calculated from the formula:

$$k_1 = (1/t)\ln\{a/(a-x)\}$$

in which a was the initial concentration of ditosylate and x was the concentration of sulfonic acid liberated at time t.

Results and Discussion

The solvolysis of the di-tosylates will proceed substantially in two steps as described below, and therefore a real solvolysis rate constant for each of them is not shown by the averaged value of the rate constants calculated from the formula. In fact, a calculated rate constant increased gradually during the alcoholysis and the acetolysis, and decreased gradually during the alcoholysis in the presence of a small amount of sodium alcoholate, in agreement with the behavior of 3-methylcyclohexyl *p*-tosylate and 1,3-di-*p*-toluenesulfoxycyclohexanes previously reported[1]. But, in all cases, since the differences between the rate constants and the averaged rate constant in the solvolysis were within 5%, the solvolysis could be approximately expressed as the first order reaction. Table I lists the data for a run with *cis*-1,4-ditosylate in acetic acid. It is seen that, though the first order rate constant increases gradually during the solvolysis, it is approximately constant.

The mean rate constants of the acetolysis of the 1,4-ditosylates were not substantially changed by the addition of a small quantity

1) N. Mori, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **80**, 1458 (1959).
2) N. Mori, This Bulletin, **33**, 1332 (1960).
3) N. Mori, ibid., **33**, 1144 (1960).
4) R. Criegee and H. Stanger, *Ber.*, **69**, 2753 (1936).
5) L. N. Owen and P. A. Robins, *J. Chem. Soc.*, **1949**, 320.

Table I. Acetolysis of *cis*-1,4-di-*p*-toluenesulfoxycyclohexane at 99.8°C

Time, min.	Ditosylate, mol. $\times 10^2$	$k_1 \times 10^2$/min.
0.0	1.03	
40.0	0.92	0.269
100.0	0.786	0.267
160.0	0.666	0.269
280.0	0.448	0.294
400.0	0.304	0.303
		Mean 0.280

of anhydrous sodium acetate, and therefore the acetolysis is predominantly of the unimolecular type. On the other hand, since the mean rate constants of the alcoholysis were decreased by the addition of sodium alcoholate, and under this condition the rate constant decreased during the solvolysis as described above, a part of the alkaline alcoholysis consists of the bimolecular displacement and elimination reactions based on a back-side attack on carbon and hydrogen coincident with the departure of the toluenesulfoxyl group. The rate constants and the relative rates for the isomeric di-tosylates are summarized in Tables II and III.

Table II. Rate constants of solvolysis of di-*p*-toluenesulfoxycyclohexanes

Position of tosyl groups	Tosylate, mol./l.	Solvent	Alkali, mol./l.	$k_1 \times 10^2$/min.
cis-1,4	0.005	M	0.020 a	2.8
〃	0.005	M	0.013 a	1.7
〃	0.005	M		1.1
〃	0.010	A	0.023 b	0.292
〃	0.010	A		0.280
trans-1,4	0.005	M	0.018 a	1.7
〃	0.005	M	0.013 a	1.5
〃	0.005	M		1.2
〃	0.010	A	0.023 b	0.603
〃	0.010	A		0.614
cis-1,2	0.005	E	0.015 c	0.39
trans-1,2	0.005	E	0.015 c	0.069
cis-1,3[1]	0.010	E	0.025 c	1.5
〃	0.010	A	0.026 b	0.195
trans-1,3[1]	0.010	E	0.025 c	3.5
〃	0.011	A	0.027 b	0.209
trans-4-acetoxy cyclohexyl tosylate[2]	0.026	A		1.61

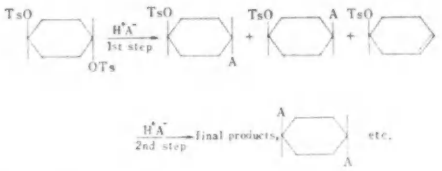
A, acetic acid; M, methanol; E, ethanol; a, sodium methoxide; b, sodium acetate; c, sodium ethoxide.

Table III. Relative rates of solvolysis of 1,4-di-*p*-Toluenesulfoxycyclohexanes

	MeOH[a]	MeOH[b]	MeOH[c]	AcOH[d]	AcOH[e]
k_{cis}	10.0	6.0	4.0	1.04	1.0
k_{trans}	2.8	2.4	2.0	0.98	1.0
k_{cis}/k_{trans}	1.6	1.1	0.9	0.48	0.45

a, contained sodium methoxide in 0.02 mol./l.
b, contained sodium methoxide in 0.013 mol./l.
c, not contained alkali.
d, contained sodium acetate in 0.023 mol/l.

Mechanism of Solvolysis.—The solvolysis of the ditosylates proceeds substantially in two steps where in the first step three monotosylates are produced and in the second step they are converted into final products. For example, in the case of *trans*-1,4-ditosylate, the process is illustrated by the following formula:



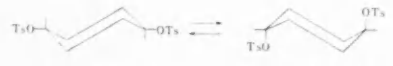
where H^+A^- is the solvent and Ts is the tosyl group.

In the present work, it has been observed that a calculated rate constant increased gradually during the neutral alcoholysis and the acetolysis. The increase in the rate constants is probably due to the fact that the reaction rate in the second step is higher than that in the first step, as explained for the similar behavior of 1,3-di-*p*-toluenesulfoxycyclohexanes[1]. This suggestion is supported for example by the experimental facts that the acetolysis rate of *trans*-4-acetoxycyclohexyl *p*-tosylate is 1.7 times that of the *trans*-1,4-ditosylate and 3.4 times that of the *cis*-1,4-ditosylate, and that 2-acetoxycyclohexyl *p*-tosylates[6] and 2-hydroxycyclohexyl *p*-brosylates[3] are rapidly solvolyzed, but 1,2-ditosylates are not acetolyzed.

Relative Rate k_{cis}/k_{trans}.—The relation between conformation and reactivity in a rigid cyclohexane system is very important. An axial group is sterically more strained and therefore, in general, more ionizable or easier to depart than an equatorial group. In the labile cyclohexane system, the trans form of cyclohexyl *p*-tosylate with a group such as the acetoxyl group[6] at the β-position is solvolyzed more rapidly than the cis isomer, but *trans*-2-substituted cyclohexyl *p*-tosylates and *p*-brosylates with a group such as *p*-bromobenzenesulfoxyl[6], nitroxyl[7], and hydroxyl[3] group are solvolyzed at a slightly faster or slower rate than the corresponding cis forms. *trans*-3-Alkyl[8],

6) S. Winstein, E. Grunwald and L. L. Ingraham, *J. Am. Chem. Soc.*, **70**, 821 (1948).
7) S. J. Cristol and B. Franzus, ibid., **79**, 2488 (1957).
8) S. Winstein and H. J. Holmess, ibid., **77**, 5562 (1955).

hydroxy[1], acetoxy[1] or methoxycarbonyl[9] cyclohexyl *p*-tosylate is solvolyzed more rapidly than the corresponding cis from. Further, *cis*-4-alkylcyclohexyl *p*-tosylate is solvolyzed more rapidly than the trans form[8]. The *trans*-1, 4-ditosylate has the two possible chair conformations as follows:



trans (e, e) trans (a, a)

The trans (e, e) is more stable than the trans (a, a). On the other hand, the cis form has only one chair conformation as follows:

cis (e, a) cis (a, e)

where Ts is the toluenesulfonyl group.

Similarly, also in the case of the 1, 2-ditosylates, the cis form has two chair conformations and the trans form only one. From those facts it is expected that the solvolysis rates of the *cis*-1, 2- and 1, 4-ditosylates are higher than that of the corresponding trans forms.

In the present work, the 1, 2-ditosylates were not solvolyzed in acetic acid after being heated for 20 hr. at 100°C, as reported by Criegee[1]. They were, however, sowewhat ethanolyzed and especially solvolyzed more rapidly in the presence of sodium alcoholate and the relative rate k_{cis}/k_{trans} was 5.6 (see Table II). Winstein[9] reported that the relative rate of acetolysis (75°C) of 1, 2-dibromobenzenesulfoxycyclohexanes was 1.1, although the rate constants of those brosylates were very low. Those facts are in agreement with the expectation described above.

In the solvolysis of the 1, 4-ditosylates, the trans form was solvolyzed in acetic acid unexpectedly at a rate 2.2 times faster than the cis form. Also, a similar result was obtained in the acetolysis of 1, 4-dibromobenezenesulfoxycyclohexanes[10] and the ratio of k_{cis} to k_{trans} was 0.78. Those facts are substantially similar to the results previously obtained in the solvolysis of 4-hydroxy- and 4-acetoxycyclohexyl tosylates[2], and are not explained by the rule as described above. Up to the present, the author can not give reasons for the fact that the trans form was acetolyzed more rapidly than the cis form. However, the methanolysis of the ditosylates, especially in the presence of alkali, proceeded more rapidly than their acetolysis and the cis form was methanolyzed more rapidly than the trans form. Thus, the ratio of k_{cis} to k_{trans} was 0.9 in methanol without alkali, 1.1 in methanol with NaOMe in 0.013 mol./l. and 1.6 in methanol with NaOMe in 0.02 mol./l.

Solvent and Alkali Effects.—In general, in unimolecular reaction solvation with solvent is very important, and the solvolysis rate in acetic acid is higher than that in ethanol. Further, such an enhancement in the rate in going from ethanol to acetic acid is nicely shown in the case of unsubstituted and substituted cyclohexyl tosylates. For example, the ratio of k_{EtOH} to k_{AcOH} for the cis form (with a-tosyl group) of 4-*tert*-butylcyclohexyl tosylate is 0.87 and that for the trans form (with e-tosyl group) 0.72[5]. On the other hand, primary alkyl tosylates, which are sensitive to a nucleophilic attack, are more reactive in ethanol than in acetic acid, such as those shown by the solvent-rate sequences[11] (EtOH : AcOH) for MeOTs, EtOTs and *iso*-BuOTs respectively to be 80 : 1, 39 : 1 and 6.2 : 1 at 75°C.

Furthermore, a carbon atom having an a-tosyl group is more easily attacked by a nucleophilic agent than that having an e-tosyl group, and the bimolecular reaction[12] of *cis*-*tert*-butylcyclohexyl tosylate with phenolate ion proceeds more rapidly than that of the trans form.

In the present work, however, the ditosylates were solvolyzed more rapidly in alcohol, especially in the presence of alkali, than in acetic acid and the solvolysis rate of the cis forms with the a-tosyl group was enhanced more than that of the trans forms without such a group, in going from acetic acid to alcohol containing alkali. Therefore, the alcoholysis and the alkaline alcoholysis of the di-tosylates probably involve bimolecular nucleophilic attack on carbon or hydrogen in the rate-determining step, similar to the primary alkyl tosylates, but in contrast to the general cyclohexyl tosylates.

Summary

Rates of solvolysis of *cis*- and *trans*-1, 2- and -1, 4-di-*p*-toluenesulfoxycyclohexanes were measured at 99.8°C in methanol or in acetic acid. In all cases, the solvolysis was approximately of first order.

Mean rate constants of the solvolysis increased in going from acetic acid to alcohol, and were enhanced by the addition of a small

9) D. S. Noyce and H. J. Weingarten, ibid., **79**, 3103 (1957).

10) N. Mori, unpublished work. The k_1 of the cis form was 1.13 and that of the trans form 1.44 at 99.8°C.

11) S. Winstein and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1120 (1952).

12) E. L. Eliel and R. S. Ro, ibid., **79**, 5995 (1958).

amount of alkali, in agreement with the behavior in solvolysis of primary alkyl tosylates.

The 1, 2-isomers were not solvolyzed in acetic acid in 20 hr., and in ethanol containing EtONa in 0.02 mol./l., the ratio of k_{cis} to k_{trans} was 5.6.

In the case of the 1, 4-isomers, the ratio was ca. 0.5 in acetic acid, 0.9 in methanol without alkali, 1.1 in methanol with MeONa in 0.013 mol./l. and 1.6 in methanol with MeONa in 0.02 mol./l.

The author wishes to express his hearty thanks to Professor Y. Tsuzuki for his advice.

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Phase Relationship in System $3CaO \cdot P_2O_5$-MgO-SiO_2

By Toshiyuki SATA

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The author already presented in 1958 the result of a study on system $3CaO \cdot P_2O_5$–$MgO \cdot SiO_2$–SiO_2 in this Bulletin[1]. This is a partial system at high silica portion in the three-component system $3CaO \cdot P_2O_5$–MgO–SiO_2. The present report concerns a basic portion in the system $3CaO \cdot P_2O_5$–MgO–SiO_2, and its phase relationships are important for the study of a composition of fused phosphate fertilizer[2] and a corrosion problem of magnesia-containing basic refractories against the molten fertilizer. This report consists of four parts; system $3CaO \cdot P_2O_5$–MgO, system $3CaO \cdot P_2O_5$–$2MgO \cdot SiO_2$, system $3CaO \cdot P_2O_5$–MgO–$2MgO \cdot SiO_2$, and the synthesis of these to system $3CaO \cdot P_2O_5$–MgO–SiO_2. Phase equilibria studies in these systems have never been published in any paper.

Experimental

Tricalcium phosphate ($3CaO \cdot P_2O_5$), forsterite ($2MgO \cdot SiO_2$), and magnesia (MgO) were used as raw materials. The first was prepared by the reaction of calcium carbonate with phosphoric acid at 1350°C as mentioned in the previous paper[1]. The second was prepared by calcining the stoichiometric mixture of magnesia and silica constituents at 1300°C. The magnesia and silica fired from 1200 to 1300°C were used as raw materials respectively. After weighing, the batches were thoroughly mixed in an agate mortar with some methyl alcohol until they became dry. They were heated in a platinum crucible or in a platinum envelope above their melting points. Then they were rapidly cooled in air or water. For batches having the melting point above 1600°C, perfect glassification was impossible. These mixing, heating, and quenching processes were repeated once more.

The silicon carbide resister furnace with an inner diameter of 25 mm. was used for this study. The sample in a platinum envelope (8×8 mm.) was suspended by a platinum wire (0.5 mm. in diameter, 200 mm. in length) at the center of the furnace tube, and quenched together with the wire in water after holding for some minutes at constant temperature (±1°C). For measuring the temperature, two kinds of thermocouples (Pt–PtRh 10% and PtRh 5%–PtRh 20%) were used. These were calibrated with the melting point of silver, copper, diopside, and palladium.

The quenched samples were powdered and examined by a polarizing microscope and by an X-ray diffractometer. Pure silicon metal was used as a standard material in X-ray examination, its accuracy being ±0.003 Å.

Results and Discussion

System $3CaO \cdot P_2O_5$–MgO. — In the first place, specimens slowly cooled from 1650°C were examined in their microstructure. The specimen containing 3.20% of MgO consisted of a primary crystal part of β-tricalcium phosphate and an eutectic part which is a turbid phase containing periclase spots surrounded by tricalcium phosphate matrix. The specimen containing 5.28% of MgO revealed the eutectic structure only. The specimen containing 7.98% of MgO consisted of the eutectic part and large periclase grains. The softening temperatures of small cones of these three compositions were measured on platinum plates in the usual way. It was found that their temperatures decreased in order of contents of MgO ranging from 1620 to 1530°C.

1) T. Sata, This Bulletin, **31**, 408 (1958).
2) T. Sata and R. Kiyoura, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **62**, 63 (1959).

TABLE I. QUENCHING DATA IN THE SYSTEM $3CaO \cdot P_2O_5$–MgO

No.	Composition			Holding		Phases present
	C_3P wt. %	MgO wt. %	MgO mol. %	temp. °C	time min.	
193	99	1.0	7.2	1470	60	β-C_3P, α-C_3P
19	98.58	1.42	10.0	1450	60	β-C_3P
20	96.8	3.2	20.0	1568	15	β-C_3P, small α-C_3P, periclase, glass
				1450	60	β-C_3P, periclase
21	94.7	5.3	30.0	1568	15	β-C_3P, periclase
22	92.1	7.9	40.0	1568	15	β-C_3P, periclase
				1555	10	〃
				1524	10	〃

The subsequent quenching runs, as listed in Table I, indicated that the specimen containing 3.20% of MgO, quenched from 1568°C, consisted of tricalcium phosphate (β and small amount of α), periclase, and glass. It is estimated from these results that this $3CaO \cdot P_2O_5$–MgO system is a binary one and its eutectic occurred at a composition of 4~7% of MgO and at a temperature near 1570±20°C, as shown in Fig. 1.

It is noted from Fig. 2, in which some X-ray diffraction lines of β-tricalcium phosphate quenched from 1450°C are plotted, that 15±3 mol. % of MgO is apparently dissolved into β-tricalcium phosphate as a solid solution. Another fact is that the transition temperature of β-α modification is considerably elevated nearly to 1550°C with increasing magnesia contents. These facts concerning tricalcium phosphate are difficult to discuss further without direct examination by a high-temperature X-ray technique. There is a new presentation of super α-$3CaO \cdot P_2O_5$ phase by Nurse et al.[3]

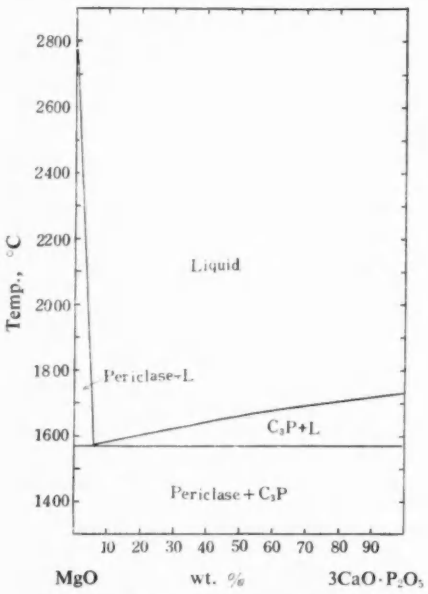

Fig. 1. The system $3CaO \cdot P_2O_5$–MgO.

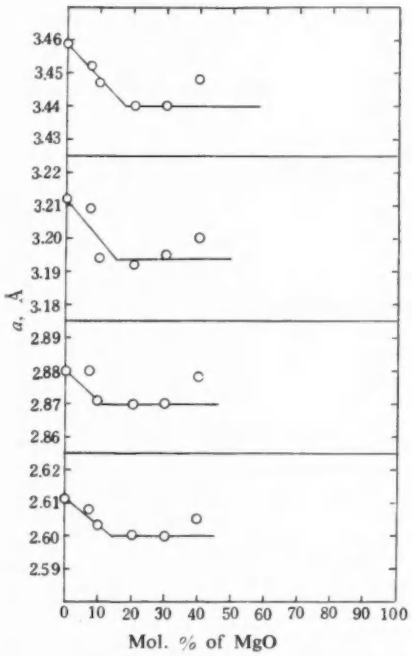

Fig. 2. The change in spacings of β-tricalcium phosphate at 1450°C in the system $3CaO \cdot P_2O_5$–MgO.

System $3CaO \cdot P_2O_5$–$2MgO \cdot SiO_2$. — Fasting and Haroldsen[4] have made X-ray tests of specimens in this system fired at 1000~1500°C, and Bobrownicki and Swiecki[5] have measured

3) R. W. Nurse, J. H. Welch and W. Gutt, *J. Chem. Soc.*, **1959**, 1077.
4) J. P. Fasting and H. Haroldsen, *Tid. Kjemi., Bergvesen Met.*, 3, 48 (1943); *Chem. Abstr.*, **39**, 13419 (1945).
5) W. Bobrownicki and Z. Swiecki, *Bull. Acad. Polon. Sci., Classe* III, 3, 232 (1955); *Chem. Abstr.*, **49**, 15419 (1955).

TABLE II. QUENCHING DATA IN THE SYSTEM $3CaO \cdot P_2O_5$–$2MgO \cdot SiO_2$

No.	Composition wt. % C_3P	Composition wt. % M_2S	Holding temp. °C	Holding time min.	Phases present
191	98	2	1342	60	β-C_3P only
75	95	5	1370	60	β-C_3P, gl.
			1340	40	β-C_3P
			1290	120	β-C_3P
			1242	180	β-C_3P, faint forst.
192	93	7	1342	60	β-C_3P only
71	90	10	1517	30	α-C_3P, β-C_3P, gl.
			1467	60	α-C_3P, β-C_3P, gl.
			1442	50	β-C_3P, α-C_3P, gl.
			1392	60	β-C_3P, gl.
			1372	540	β-C_3P, gl.
			1340	40	β-C_3P
			1312	40	β-C_3P
			1290	40	β-C_3P, forst.
70	80	20	1545	20	Ng., gl.
			1442	20	Ng., gl.
			1392	60	Ng., β-C_3P, gl.
			1372	60	β-C_3P, Ng., gl.
			1357	40	β-C_3P, gl.
			1352	300	β-C_3P, forst., small gl.
			1342	60	β-C_3P, forst.
72	75	25	1575	15	gl.
			1566	15	Ng., gl.
			1515	15	Ng., gl.
			1374	40	β-C_3P, Ng., gl.
			1352	40	β-C_3P, forst.
73	72.5	27.5	1548	15	Ng., gl.
			1528	15	Ng., gl.
			1442	60	Ng., gl.
			1382	40	β-C_3P, Ng., gl.
			1372	40	β-C_3P, Ng., forst., gl.
			1365	50	β-C_3P, forst., small gl.
			1352	40	β-C_3P, forst.
66	70	30	1398	40	gl.
			1392	40	β-C_3P, Ng., faint forst., gl.
			1372	40	β-C_3P, Ng., forst., gl.
			1347	40	β-C_3P, forst.
74	67.5	32.5	1432	60	gl.
			1407	50	β-C_3P, small forst., gl.
			1374	40	β-C_3P, forst.
67	60	40	1465	40	gl.
			1458	20	forst. gl.
			1452	40	Ng., forst., gl.
			1400	60	Ng., small forst.
			1382	50	Ng., forst.
			1342	60	β-C_3P, forst.
			1300	60	β-C_3P, forst.
68	50	50	1537	20	gl.
			1522	20	forst., gl.
			1507	20	forst., gl.
			1442	60	Ng., forst., gl.
69	40	60	1442	60	Ng., forst., gl.

Abbreviations: $C_3P = 3CaO \cdot P_2O_5$, $M_2S = 2MgO \cdot SiO_2$, Ng. = nagelschmidtite
forst. = forsterite, gl. = glass.

the softening points of this system. But the phase relationships of this system have not been presented.

Results of the quenching runs of this two-component system are summarized in Table II, from which a preliminary phase diagram of this system was obtained as shown in Fig. 3. Nagelschmidtite[6] (which was identified by a hexagonal X-ray pattern similar to that in $3CaO \cdot P_2O_5$–$2CaO \cdot SiO_2$ system) appeared over a wide range of this system above a temperature of 1350°C, and was crystallized primarily in the composition range of $3CaO \cdot P_2O_5$ side.

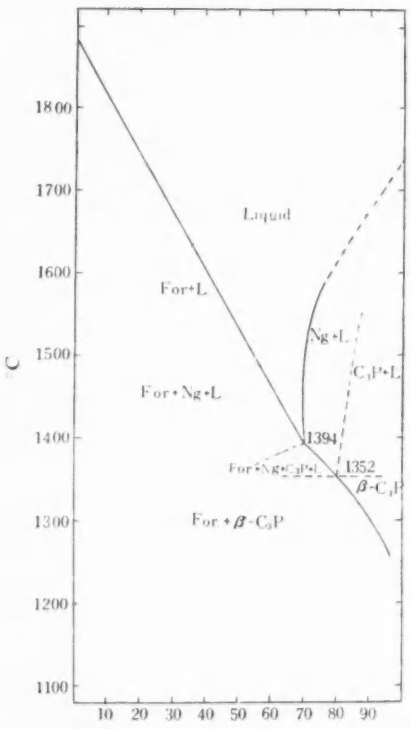

Fig. 3. The system $3CaO \cdot P_2O_5$–$2MgO \cdot SiO_2$.

The liquidus line falls very steeply to a temperature minimum at 1394°C and a composition of 70% $3CaO \cdot P_2O_5$ and 30% $2MgO \cdot SiO_2$. Below this temperature 1394°C, the secondary crystallization temperature of forsterite from nagelschmidtite and liquid decreases. Below 1352°C, nagelschmidtite and liquid disappeared, and forsterite and β-tricalcium phosphate phase only appeared. The meaning of this disappearance temperature 1352°C is not clear now. β-Tricalcium phosphate seems to contain magnesia component, judging from the fact that the crystallization temperature of forsterite from β-tricalcium phosphate phase descends with increasing contents of $3CaO \cdot P_2O_5$, and d-spacings of β-tricalcium phosphates in their X-ray patterns decrease till the content of 15 mol. % (7.4 weight %) of $2MgO \cdot SiO_2$ is attained, as shown in Fig. 4. Below about 1200°C, this two-component system is a binary one consisting of forsterite and β-tricalcium phosphate.

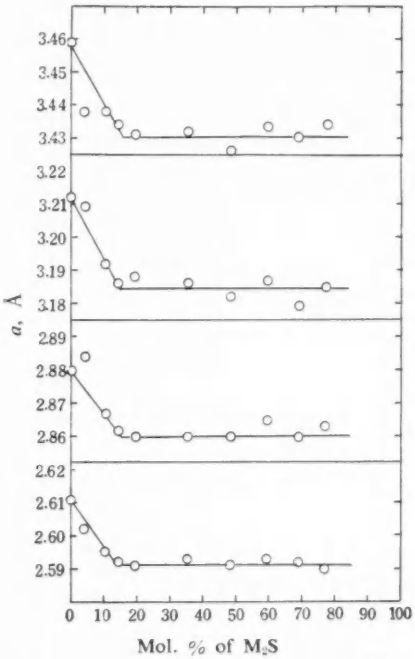

Fig. 4. The change in spacings of β-tricalcium phosphate in the system $3CaO \cdot P_2O_5$–$2MgO \cdot SiO_2$.

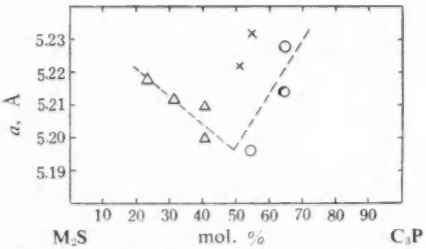

Fig. 5. The change in lattice constants of nagelschmidtite in the system $3CaO \cdot P_2O_5$–$2MgO \cdot SiO_2$ at 1370~1490°C.
○ Ng.+L, △ Ng.+forst.+L,
× Ng.+β-C_3P+L

6) G. Nagelschmidt, *J. Chem. Soc.*, **1937**, 865.

When the lattice constants *a* of hexagonal negelschmidtite are calculated from their (110) peak and plotted against molar compositions, a valley-type change are obtained, whose bottom may occur at the composition of temperature minimum of liquidus as shown in Fig. 5.

From the results mentioned above, this system was found to be complex, owing to the formation of nagelschmidtite above 1350°C, below which it is considered to be binary.

System $3CaO \cdot P_2O_5$ – MgO – $2MgO \cdot SiO_2$. — Although all of the specimens of this system slow-cooled to room temperature consisted of β-tricalcium phosphate, periclase, and forsterite, the primary crystal in the area of high content of $3CaO \cdot P_2O_5$ was nagelschmidtite, being the same as that mentioned in the system $3CaO \cdot P_2O_5$–$2MgO \cdot SiO_2$. But it was found by the preliminary quenching test that a ternary eutectic among their three components seems to be present. This paragraph described results of quenching experiments made to decide the position of a three-component eutectic.

The twelve compositions, which are expected to locate near the eutectic, were taken on the two tie lines connecting No. 24 ($60C_3P$–40M) with No. 72 ($75C_3P$–$25M_2S$) and No. 74 ($67.5C_3P$–$32.5M_2S$) along the C_3P–M_2S join, as represented in Fig. 6. Results obtained are listed in Table III, from which a eutectic position was graphically decided to locate at the composition of 70% $3CaO \cdot P_2O_5$, 21% MgO and 9% SiO_2, and at 1362±5°C.

This eutectic temperature is close to the transition point between nagelschmidtite and β-tricalcium phosphate. It was, however, found that β-tricalcium phosphate was present at this eutectic temperature. The primary field of nagelschmidtite was approximately estimated as a dotted boundary from the previous results of the investigation in the systems C_3P–MS and C_3P–M_2S. The facts that a small amount of periclase was present even in the specimens quenched above liquidus temperatures of all compositions, and that nagelschmidtite was present even in the primary field of periclase or forsterite above eutectic

Table III. Quenching data in the system $3CaO \cdot P_2O_5$–MgO–$2MgO \cdot SiO_2$

No.	Composition wt. %		C_3P	M wt. %	S	Holding temp. °C	Holding time min.	Phases present (peri. = periclase)
	No. 74	No. 24						
78	95	5	67.1	19.7	13.2	1442	60	gl. (faint peri.)
						1407	40	small forst., peri., gl.
						1364	60	β-C_3P, forst., peri.
80	90	10	66.8	20.7	12.5	1442	60	small peri., gl.
						1412	50	small forst., gl.
						1392	50	β-C_3P, forst., gl.
81	85	15	66.4	21.8	11.8	1407	50	small peri., gl.
						1382	50	β-C_3P, small forst., gl.
82	80	20	66.0	22.9	11.1	1422	40	gl.
						1392	60	peri., gl.
						1382	50	β-C_3P, forst., gl.
83	75	25	65.6	24.0	10.4	1390	50	peri., gl.
						1382	50	β-C_3P, forst., peri., gl.
101	65	35	64.9	26.1	9.0	1382	40	peri., gl.
						1372	40	peri., β-C_3P, forst.
102	55	45	64.2	28.2	7.6	1365	20	peri., gl.
						1356	60	peri., β-C_3P, forst.
103	45	55	63.3	30.4	6.3	1375	40	peri., gl.
						1356	40	β-C_3P, forst., peri.
104	35	65	62.6	32.5	4.9	1356	50	β-C_3P, forst., peri.
	No. 72	No. 24						
151	90	10	73.5	16.9	9.6	1372	60	peri., gl.
152	80	20	72.0	19.5	8.5	1398	40	Ng., peri., gl.
						1372	50	Ng., peri., gl.
						1369	40	β-C_3P, peri., forst., gl.
						1364	25	no gl.
153	70	30	70.5	22.0	7.5	1372	60	peri., Ng., gl.
						1364	40	peri., β-C_3P, forst., gl.

temperature, were neglected in drawing this phase diagram at the step of this study, Detailed studies of the system containing nagelschmidtite will be made in future, because of the interesting scope of nagelschmidtite structure (super α-tricalcium phosphate by Nurse or its solid solution containing MgO and SiO_2).

System $3CaO \cdot P_2O_5$–MgO–SiO_2. — The preliminary phase diagram, as shown in Fig. 6, was obtained from the results of previous paragraphs and the separate report of the system $3CaO \cdot P_2O_5$–$MgO \cdot SiO_2$–SiO_2[1]. The probable boundary curve between the phosphate and the forsterite fields in the $3CaO \cdot P_2O_5$–$2MgO \cdot SiO_2$–$MgO \cdot SiO_2$ triangle was drawn from the results without a cooling experiment.

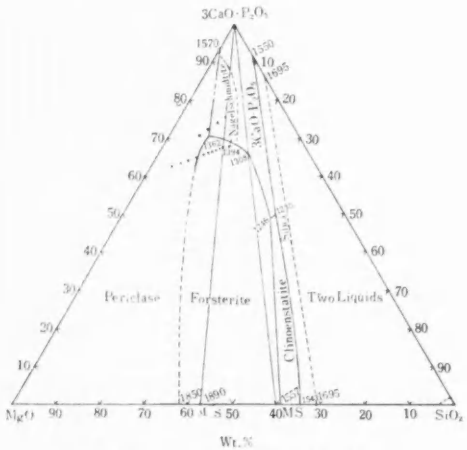

Fig. 6. The system $3CaO \cdot P_2O_5$–MgO–SiO_2.

Summary

The phase relationship in the system $3CaO \cdot P_2O_5$–MgO–SiO_2 was investigated by a cooling experiment in the usual manner. The system $3CaO \cdot P_2O_5$–MgO, a side of this triangle, is a simple binary one, its eutectic being located at the composition of 4~7% by weight of magnesia and 1570±20°C. The system $3CaO \cdot P_2O_5$–$2MgO \cdot SiO_2$ is not binary over the temperature of about 1350°C, below which it is considered as binary. Above 1350°C, nagelschmidtite is formed over the whole composition range and crystallized primarily from liquid at a high $3CaO \cdot P_2O_5$ portion. The minimum liquidus temperature is 1394°C, which is located at the composition of 70% C_3P and 30% M_2S. The system $3CaO \cdot P_2O_5$–MgO–$2MgO \cdot SiO_2$ was considered to be complex owing to the presence of nagelschmidtite, but the eutectic among their three components is located at the composition of 70% $3CaO \cdot P_2O_5$, 21% MgO, and 9% SiO_2, and 1362±5°C.

From the results described above and from those of the author's previous reports, the preliminary phase diagram of the system $3CaO \cdot P_2O_5$–MgO–SiO_2 was constructed. In this diagram the problem that nagelschmidtite is formed in the composition range which is rich in $3CaO \cdot P_2O_5$ was not mentioned in detail. In addition to this, it was found by X-ray examination that β-tricalcium phosphate may be apparently stabilized at a higher temperature than β-α transition point, and has the appearance of dissolving magnesia component.

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Interactions of Surface Active Agents with Congo Red

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Interactions between various surface active agents and many substances such as protein, dyes and polymers have been studied for contribution to the elucidation of fundamental properties of surface active agents to or extend their applications[1-4]. It has been reported that some dyes such as azo, thiazine or triphenylmethane dyes were changed in their spectra with the addition of various substances such as agar, chondroitin sulfate, nucleic acid or albumin[5-9]. The similar effects of surface active agents, though the greater part of these are ionic ones, on the spectral changes of some dyes have also been studied in recent years[10-15]. In the case of non-ionic detergents, a complex formation has been predicted between dyes and detergents[12,15], but details are not known.

In this paper, the metachromatic effects of a non-ionic surface active agent, Tween 80 and a cationic one, cetyl pyridinium chloride on the absorption spectrum of Congo Red solution are reported.

Experimental

Reagents.—The Congo Red used in this experiment was purified by salting out with sodium acetate and recrystallizing several times from water. Tween 80 (Atlas Powder Co.) was dissolved in water to about 5%, ionic impurities were removed by means of ion-exchange resins (Amberlite IR-120, IRA-400), then evaporated and dried in vacuo at about 50°C. Other reagents were recrystallized from water before use.

Absorption Spectra.—The absorption spectra of the solutions were measured with a Beckman type spectrophotometer using a 1 cm. glass absorption cell.

Procedures.—The procedure used in the preparation of the dye solutions to be measured was as follows: 1 ml. of the Congo Red stock solution (2.34×10^{-3} mol./l.) was measured in a 100 ml. volumetric flask. Then 1 ml. of the concentrated buffer solution was pipetted in and an appropriate amount of 4.9% Tween 80 solution was added to the flask to obtain the desired pH and detergent concentrations. The entire contents of the flask were then diluted to 100 ml. and stirred sufficiently. It was left to stand for about 30 min. after the preparation in order to secure an equilibrium (it had been confirmed that 30 min. was sufficient for the equilibrium), then the spectrum was measured using an aliquot part of the solution. Another part of solution was used to determine the pH of the solution. In the experiments of cetyl pyridinium chloride, the sample solutions prepared were centrifuged and then the supernatant solutions were used to measure the spectra.

Results

Fig. 1 represents the absorption spectra of Congo Red solution of 2.34×10^{-5} mol./l. in the presence of various amounts of Tween 80 at the fixed pH of 3.4. The spectrum varies gradually with the addition of Tween 80 and the new absorption peak appears at about 510 mμ. This peak increases in height with increasing concentration of Tween 80 and it becomes constant above the Tween 80 concentration of 0.309%. The isosbestic point is clearly observed among these spectra, which may suggest that there is a definite molecular constitution of the product. An isosbestic point of this kind was also observed in other reports[2,13,15] which studied the interaction between some dyes such as Methyl Orange, Benzopurpurine 4B and Erythrosine and non-ionic or cationic detergents.

Fig. 2 shows the results measured at pH 4.3. As a whole the spectra are similar to those in Fig. 1, but the spectral change occurs with the addition of a smaller amount of Tween 80 than in the case of that at pH 3.4. The wavelength of the absorption peak of the product is the same in both cases.

Fig. 3 shows the change of the absorbance at the absorption peak with the concentration

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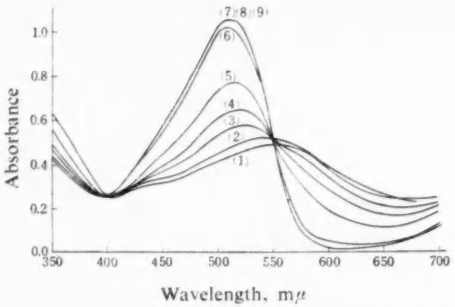

Fig. 1. Absorption spectra of Congo Red solutions containing various amounts of Tween 80 at fixed pH of 3.4; concentration of Congo Red, 2.34×10^{-5} mol./l.; concentration of Tween 80 (%): (1), 0.00; (2), 0.00483; (3), 0.0193; (4), 0.0386; (5), 0.078; (6), 0.155; (7), 0.309; (8), 0.525; (9), 1.05.

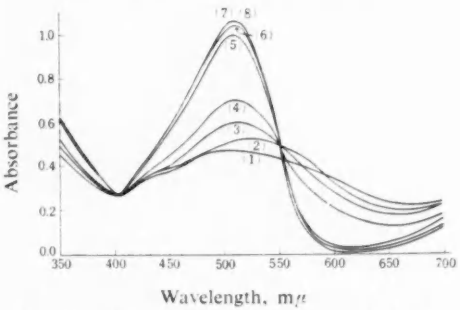

Fig. 2. Absorption spectra of Congo Red solutions containing various amouts of Tween 80 at pH 4.3; concentration of Congo Red, 2.34×10^{-5} mol./l.; concentration of Tween 80 (%): (1), 0.00; (2), 0.005; (3), 0.02; (4), 0.04; (5), 0.08; (6), 0.15; (7), 0.29; (8), 0.58.

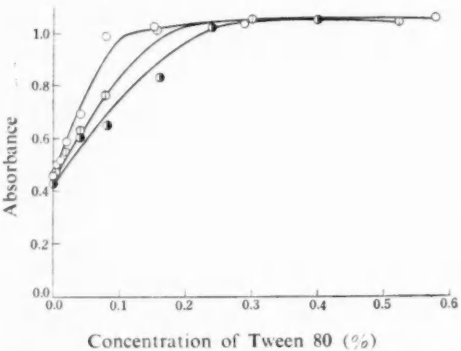

Fig. 3. The absorbances at 510 mμ of Congo Red solutions plotted against increasing concentrations of Tween 80 at three values of pH; ◑ pH 3.0; ◌ pH 3.4; ○ pH 4.3.

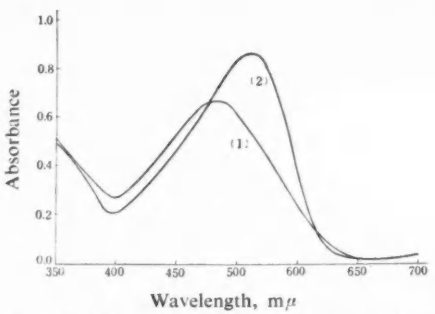

Fig. 4. Effect of the addition of Tween 80 on the absorption spectrum of Congo Red solution at pH 7.0; concentration of Congo Red, 1.87×10^{-5} mol./l.; conccentration of Tween 80 (%): (1), 0.00; (2), 0.35.

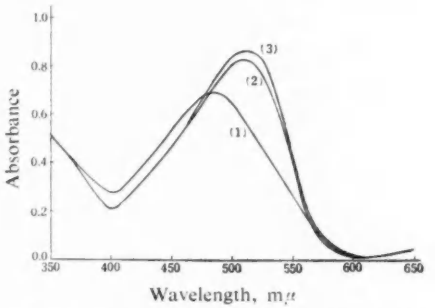

Fig. 5. Effect of the addition Tween 80 on the absorption spectrum of Congo Red solution at pH 9.2; concentration of Congo Red, 1.87×10^{-5} mol./l.; concentration of Tween 80 (%): (1), 0.00; (2), 0.016; (3), 0.16.

of Tween 80 at three values of pH of the dye solution.

The identical effects of Tween 80 are also observed in either the neutral or basic medium, the results being shown in Figs. 4 and 5. In these cases the absorbance at 510 mμ became constant with the addition of a very small amount of the detergent and their spectral changes were not remarkable as compared with that in the acidic medium.

When cetyl pyridinium chloride (c. p. c.) is added to the Congo Red solution at pH 4.2, a spectral shift occurs and indicates the presence of an interaction product between c. p. c. and Congo Red, as shown in Fig. 6. In this case, Congo Red is dispersed by a small quantity of c. p. c., and has an absorption peak at about 660 mμ. When the concentration of the detergent increases, a new peak appears at 460 mμ which may be assigned to the interaction product between Congo Red and c. p. c. This peak increases in height with increasing

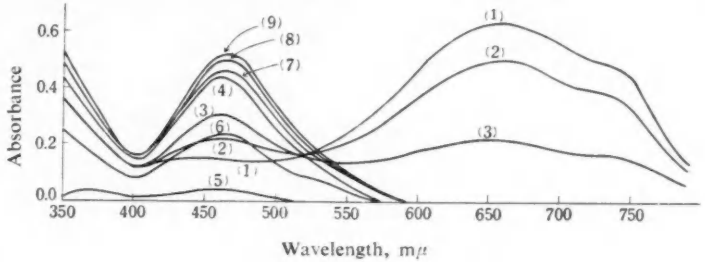

Fig. 6. Absorption spectra of Congo Red solutions containing various amounts of cetyl pyridinium chloride at fixed pH of 4.2; concentration of Congo Red, 2.17×10^{-5} mol./l.; concentration of cetyl pyridinium chloride (mol./l.$\times10^{5}$): (1), 0.725; (2), 1.45; (3), 2.90; (4), 3.63; (5), 4.35; (6), 10.1; (7), 11.6; (8), 14.5; (9), 160.

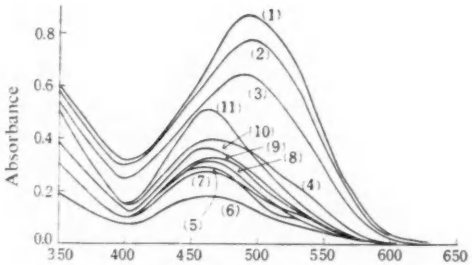

Fig. 7. Absorption spectra of Congo Red solutions containing various amounts of cetyl pyridinium chloride at fixed pH of 7.0; concentration of Congo Red, 2.17×10^{-5} mol./l.; concentration of cetyl pyridinium chloride (mol./l.$\times10^{5}$): (1), 0.00; (2), 0.685; (3), 1.37; (4), 2.74; (5), 3.43; (6), 8.22; (7), 9.59; (8), 11.0; (9), 16.4; (10), 27.4; (11), 68.5.

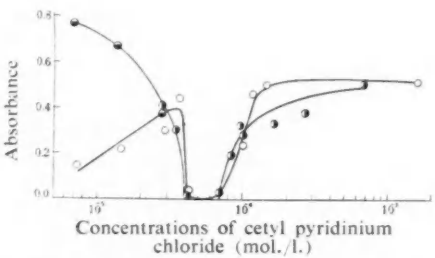

Fig. 8. The absorbances at 464 mμ and 490 mμ (pH 7.0) of Congo Red solutions (from which the precipitates are removed) plotted against the concentrations of cetyl pyridinium chloride at two values of pH: ○, 464 mμ, pH 4.2; ◑, 464 mμ, pH 7.0; ◒, 490 mμ, pH 7.0; concentration of Congo Red, 2.17×10^{-5}mol./l.

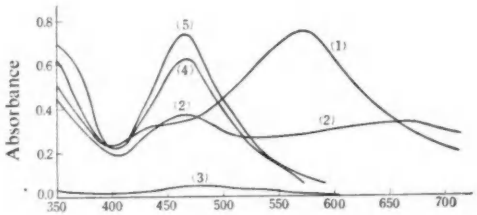

Fig. 9. Effect of the addition of cetyl pyridinium chloride at pH 3.8; concentration of Congo Red, 2.88×10^{-5} mol./l.; concentration of cetyl pyridinium chloride (mol./l.$\times10^{5}$): (1), 0.00; (2), 1.5; (3), 4.5; (4), 30.0; (5), 300.

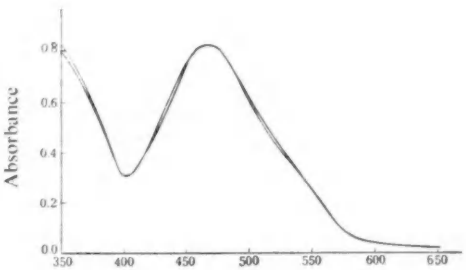

Fig. 10. Effect of the addition of cetyl pyridinium chloride at pH 1.45; concentration of Congo Red, 2.88×10^{-5} mol./l; concentration of cetyl pyridinium chloride, 7.3 and 14.5×10^{-5} mol./l.

concentration of c. p. c. The interaction products are precipitated in the presence of a certain amount of the detergent and then dispersed again with further increase of the concentration of c. p. c. The same effect of c. p. c. is observed in the neutral medium as shown in Fig. 7. In either case the interaction products are completely precipitated in the concentration range where the mole ratio of Congo Red to c. p. c. is about 1/2 and begins to be dispersed with further increase of c. p. c. concentration as shown in Fig. 8. Figs. 9 and 10 show that the same interaction product is also formed in the more acidic medium.

Discussion

The absorption peak at 510 mμ, as seen from Figs. 1, 2, 4 and 5, is considered to indicate that Congo Red and Tween 80 make a definite molecular compound irrespective of the pH of the solution. The results of Fig. 3 show that the hydrogen ion in the medium plays an important role in the equilibrium of the interaction between Congo Red and Tween 80. Either the acid or the base form of Congo Red is similarly varied in its spectrum and well dispersed by the addition of a sufficient amount of Tween 80. However, the amount of detergent required to show just sufficient change increases with lowering the pH of the medium. Although in acidic Congo Red solutions containing insufficient Tween 80 (below 0.309% of Tween 80 concentration at pH 3.4), precipitates appear by aging (about 24 hr. after preparation), in the systems containing sufficient detergent, no precipitation occurs. This is probably due to a kind of solubilization, but the precise mechanism is not known at the present.

In view of these results, it may be considered as follows: in an acidic medium, an acid form of Congo Red is equilibrated to a base form as in the following formula,

$$R\begin{matrix}NH_2\\NH_2\end{matrix} + 2H^+ \rightleftarrows R\begin{matrix}NH_3^+\\NH_3^+\end{matrix} \qquad (1)$$

It is possible to assume the following equilibrium process for the spectral change,

$$R\begin{matrix}NH_2\\NH_2\end{matrix} + 2\,\text{Tween 80} \rightleftarrows R\begin{matrix}NH_2-\text{Tween 80}\\NH_2-\text{Tween 80}\end{matrix} \qquad (2)$$

In this expression $R\begin{matrix}NH_2\\NH_2\end{matrix}$, $R\begin{matrix}NH_3^+\\NH_3^+\end{matrix}$ and $R\begin{matrix}NH_2-\text{Tween 80}\\NH_2-\text{Tween 80}\end{matrix}$ represent the base form of Congo Red, the acid one and the interaction product respectively.

The effect of pH (Fig. 3) may be interpreted qualitatively by these assumptions as follows. When the pH of the medium is lowered, the concentration of the base form decreases according to the formulation 1, which results in an increase of the amount of Tween 80 required to give a definite absorbance. In either neutral or basic medium, the same processes are probably considered to occur from the results of Figs. 4 and 5. In these cases, however, the concentrations of the base form become so great that the process is mainly represented by the formulation 2 and the same effect is produced with a smaller amount of Tween 80 than that in the acidic medium.

Thus, the amino groups of Congo Red molecule are considered to be blocked with Tween 80 and the products are well dispersed, since the aggregation of Congo Red molecules is prevented by the attachement of Tween 80. It has been observed that the adsorption of Congo Red for filter paper or cotton (which is considered to have a negative surface), was reduced remarkably by the addition of Tween 80, which may also be interpreted by a similar process.

In the case of cetyl pyridinium chloride, the wavelength of the new peak is 460 mμ, the position of which is not affected by the medium pH as shown in Figs. 6 and 7.

When the concentration of the detergent is 4.2×10^{-5} mol./l., at which the mole ratio of Congo Red to detergent is 1/2, the products are most hydrophobic and precipitated. They have a trend to be dispersed both sides of this ratio. In the lower concentrations of the detergent, in which the mole ratio is below about 1/1, neither precipitation nor metachromatic color is oberved. In the higher concentrations above the mole ratio of about 1/4, the products are well dispersed. The dispersion in the latter case is not considered to be due always to solubilization[11], since the system being dispersed with sufficient c. p. c. produces no precipitation even by means of dilution.

From these facts, it is considered that Congo Red is bound at the anionic loci, sulfonates, with c. p. c. by ionic force. It is probable that the products whose sulfonates are blocked become hydrophobic, but with further c. p. c. they will become hydrophilic again owing to the adsorption of the excess of c. p. c. with the hydrophilic groups towards water.

Summary

The spectral changes of Congo Red solution with the addition of Tween 80 and cetyl pyridinium chloride were measured at various pH.

The wavelength of the absorption peak of

the interaction product between Congo Red and Tween 80 is 510 mμ in the acidic medium as well as those in the neutral and the basic ones, from which it is considered that they produce a molecular compound of a definite constitution irrespective of the medium pH. However, since the amount of Tween 80 required to show the same effect in spectra increases with lowering pH, it is considered that only a base form of Congo Red is probably active and binds with Tween 80 at the amino groups.

The solutions of Congo Red containing sufficient cetyl pyridinium chloride have an absorption peak at 460 mμ. The product is completely precipitated as the ratio of Congo Red to cetyl pyridinium chloride is 1/2 and dispersed in both sides of this ratio, which depends little on the medium pH. This is considered to show that cetyl pyridinium chloride binds with Congo Red at the sulfonate groups, the product becomes most hydrophobic as two sulfonates in a molecule are blocked and hydrophilic with an excess of the detergent.

In conclusion, the author wishes to express his sincere thanks to Professor R. Matsuura of Kyushu University for his kind guidance and encouragement during this experiment, and also to Dr. H. Kimizuka of Kyushu University for his supply of the cationic detergent and discussion concerning this work.

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Studies on the Chemical Forms of the Recoil Products in Some Neutron-Irradiated Phosphorus Compounds

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The Szilard-Chalmers effect in the neutron-irradiated phosphorus compounds is rather complicated. This phenomenon was studied by several authors, but some important problems seem to be still left without any clear solution. In 1940, Libby[1] studied the Szilard-Chalmers effect in phosphate and phosphite, and found that phosphite is formed in neutron-irradiated phosphate. The retention of phosphate was about 50%. Thomas et al.[2] studied similar effects. In 1951, Fiskell[3] discovered some formation of hypophosphite in neutron-irradiated phosphate.

Fiskell et al.[4] continued further investigation on the Szilard-Chalmers effect of calcium phosphates, and found that pyro- and metaphosphate are formed besides hypophosphate. Aten et al[5]. also investigated the formation of the polyatomic species in several neutron-irradiated phosphorus compounds, and demonstrated the presence of pyrophosphate in the recoil products. In the papers mentioned above the precipitation method was used for the analysis of the irradiated phosphorus compounds, and therefore exact determination of the complicated products was difficult.

Recently, the technique of paperelectrophoresis has been developed and has been applied successfully to the separation of many components in the complicated system. Sellers et al.[6] studied the chemical form of the recoil products in various phosphorus compounds by this method. Sato et al.[7] further investigated the question in the same way. These authors[6,7] reported that the principal component in each case was the parent species, and besides this principal component several components appeared in the chromatogram in small percentages. They argued that neutron-irradiation of various phosphates does not bring about extensive disruption of the P–O bonds or the P–O–P linkage.

Although paper electrophoresis is an excellent method for the separation and the determination of various phosphorus compounds, it

1) W. F. Libby, *J. Am. Chem. Soc.*, **62**, 1930 (1940).
2) W. D. E. Thomas and D. J. D. Nicholas, *Nature*, **163**, 719 (1949).
3) J. G. A. Fiskell, *Science*, **113**, 244 (1951).
4) J. G. A. Fiskell, W. A. Delong and W. F. Oliver, *Can. J. Chem.*, **30**, 9 (1952).
5) A. H. W. Aten, Jr., H. van der Straaten and P. C. Riesbos, *Science*, **115**, 267 (1952).
6) P. A. Sellers, T. R. Sato and H. H. Strain, *J. Inorg. Nucl. Chem.*, **5**, 31 (1957).
7) T. R. Sato, P. A. Sellers and H. H. Strain, ibid., **7**, 84 (1959).

should be limited to the analysis of the species which are stable to the electric current and to the heat liberated on the paper for several hours. Therefore we felt it would be necessary to compare the results with those by ordinary paper chromatography. We were particularly interested in the formation of polyatomic species which might be produced by the heat liberated in the neighborhood of the recoil atom. Sato et al.[7] detected a component presumably corresponding to pyrophosphate in neutron-irradiated phosphate, but they did not show the percentage of this component. Aten et al.[7] showed that an appreciable fraction of pyrophosphate is formed from phosphate. However, the formation of higher polyphosphates than pyrophosphate might occur, but this has not been shown so far. Thus we studied the chemical form of the recoil products in the neutron-irradiated phosphorus compounds by paper chromatography, and found several new facts.

Experimental

Target Materials.—The target materials used in this work are as follows: H_3PO_4; NaH_2PO_4, $NaH_2PO_4 \cdot H_2O$, $NaH_2PO_4 \cdot 2H_2O$, $NH_4H_2PO_4$, KH_2PO_4, Na_2HPO_4, $Na_2HPO_4 \cdot 12H_2O$, $(NH_4)_2HPO_4$; Na_3PO_4, $Na_3PO_4 \cdot 12H_2O$, $Zn_3(PO_4)_2$; $Na_4P_2O_7$, $Na_4P_2O_7 \cdot 10H_2O$; $Na_2HPO_3 \cdot 5H_2O$.

These substances are guaranteed reagents of the Kanto Chemical Co. or of the Wako Pure Chemical Ind. Before the experiment the purity of each substance was tested by means of radioactivation analysis; the sample was dissolved in water (zinc phosphate was dissolved in dilute hydrochloric acid), and one drop of the solution was put on the filter paper for chromatography; this was developed with *n*-butanol which had been shaken with the same volume of 2 N nitric acid; the filter paper was dried and irradiated in a nuclear reactor; after appropriate cooling time, the radioautogram of the filter paper was prepared. Each test gave no impure component.

Irradiation.—Solid targets were irradiated in the Irradiation Hole No. 3, 12 or 15 in the nuclear reactor JRR-1 (homogeneous solution type). Hole No. 16 was used for short irradiation of solid targets. Liquid targets were irradiated in Hole No. 6. The standard thermal neutron flux in each hole is given as follows[8].

No. 3.	0.48×10^{12} n/cm²/sec.
6.	0.40 〃
12.	0.38 〃
15.	0.22 〃
16.	0.51 〃

These values were given at the operation of 40 kW. per hour. In the whole period of this work the reactor was operated at 40 kW. per hour. It is desirable to irradiate the sample in the same position of the same hole, but this could not be realized for all cases. Presumably the variation of neutron flux in these experiments will not bring about any difference in the results. In Hole No. 16 (the nearest from the reactor core) the contribution of fast neutrons to the total radioactivation was tested by the cadmium foil absorption method. The result showed that about 5% of the radioactivity was produced by fast neutrons (residual 95% by slow and thermal neutrons). In the other holes contribution of neutrons to the total radioactivation will be smaller. Perhaps the contribution of fast neutrons will not greatly affect the results in all the experiments. Except in the case of short irradiation, the targets were usually irradiated for 5 hr. a day, and for successive three days a week. The irradiation temperature did not exceed about 50°C in any of the experiments.

Analysis.—*Paper chromatography.*—The irradiated target was dissolved in water, and one drop of the solution was put on the starting point of the filter paper, Tôyô No. 53 (2 cm × 40 cm). Other sorts of filter paper such as Tôyô No. 50, 51, 51A, 52 and 54 were tested, but No. 53 gave the best results. Several developing solvents were tested, and the best results were obtained by the use of *n*-butanol which had been shaken with the same volume of 2 N nitric acid. Development was made by the one-dimensional ascending method for about 15 hr., the travelling distance being 23~27 cm.

Detection of Radioactive Zones.—After development the filter paper was dried well and the radioautogram was taken on Fuji X-ray film. For the determination of the components on the chromatogram, the paper was cut in sections of 0.5 cm. width, and the radioactivity was measured by a proportional counter (Radiation Counter Laboratories, Inc.; an end-window type; flow gas, methane; counting efficiency about 30%). When other radionuclides such as ^{24}Na and ^{42}K were produced, decay curves were investigated to distinguish them from ^{32}P.

Miscellaneous.—Experiments on the time-dependency of ^{32}P were carried out at room temperature (about 20°C) in air (under atmospheric pressure). Enrichment of ^{32}P was roughly examined by the coloration test on the chromatogram obtained. A solution of ammonium molybdate was sprayed on the filter paper. In the cases of phosphate, pyrophosphate and higher polyphosphates a yellow color appeared, and in the cases of phosphite and hypophosphite a pale blue color appeared after the filter paper was heated. Thus amounts of the phosphorus compounds were roughly estimated.

Result

There were small changes in R_f values according to the experimental condition, but they did not exceed 0.02. In Fig. 1, chromatograms of several species are shown. The R_f values of phosphate, phosphite* and pyrophosphate

8) K. Takahashi, M. Imai and Y. Kato, *JAERI-1004* (1958).

* The R_f value of hypophosphite is nearly the same as that of phosphite and they could not be distinguished from each other. The sum of these fractions are shown in the tables.

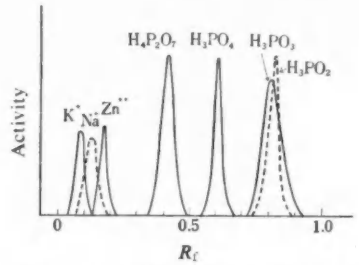

Fig. 1. R_f values of some phosphorus compounds.

were referred to in each experiment. In some cases an unknown species was developed at an R_f value of 0.95~1.0. This was usually observed as a very small spot. In almost all the experiments, spots appeared at the R_f value of 0.05~0.4. Usually these were not clear but diffused and trailing. Sometimes two or three spots appeared in these parts. On the other hand, when a disodium hydrogen phosphate sample was heated and dehydrated into pyrophosphate and higher polyphosphate, this sample always showed the spots at the R_f value of 0.05~0.4 besides a spot of pyrophosphate. Moreover, trimetaphosphate and hexametaphosphate were developed at the R_f value of 0.05~0.1. Therefore the spots at the R_f value of 0.05~0.4 were considered to be due to higher polyphosphates. In some experiments a spot appeared at the starting point of the chromatogram. This small fraction seems to be due to elementary phosphorus as was suggested by previous authors[6,7]. Oxidation of phosphorus might occur because the targets were irradiated in air. In the tables the sum of the percentages of the fractions is not always 100%, because the fractions of the tailing part of each spot, of the spot at the starting point, and of the spot at the R_f value of 0.95~1.0 are omitted. Errors shown in the tables include not only counting errors but errors based on incomplete separation of the spots.

The enrichment of ^{32}P was examined by the coloration already mentioned. Except for the target compound the chemical species which appeared in the chromatogram were not detected by the test. Comparing it with the radioactivity data in the tables, this result shows that the chemical species other than the target compound are enriched by the Szilard-Chalmers effect.

The test for radioactive gases such as phosphine and diphosphine was omitted in this work. As shown in Sellers's work[6] these were present only in a very small percentage.

Phosphoric Acid. — Liquid phosphoric acid was irradiated in Hole No. 6 (neutron flux: 0.40×10^{12}n/cm^2/sec.) in JRR-1 for 5 hr. The results are shown in Table I. Small changes in the distribution are observed with the time elapsed. Most of ^{32}P atoms are present as phosphoric acid, and small portions are present as phosphorous and pyrophosphoric acids. Phosphorous acid and pyrophosphoric acid seem to change slowly into phosphoric acid. Besides these, higher polyphosphates fractions were detected.

Potassium Dihydrogen Phosphate.—The target was irradiated in Hole No. 15 (neutron flux: 0.22×10^{12}n/cm^2/sec.) in JRR-1 for 15 hr. The results are shown in Table II.

In this experiment higher polyphosphates

Table I. Szilard-Chalmers effect in phosphoric acid

Chemical forms of ^{32}P	Time elapsed after irradiation (days)			
	1	5	8	15
	%	%	%	%
H_3PO_4	89.2±0.4	92.6±0.5	93.9±0.5	95.7±0.5
$H_3PO_3(+H_3PO_2)$	5.1±0.1	2.9±0.06	2.2±0.06	0.3±0.01
$H_4P_2O_7$	2.5±0.07	1.4±0.04	1.2±0.04	1.0±0.04
Higher polyphosporic acid	2.0±0.09	Trace	Trace	Trace

Table II. Szilard-Chalmers effect in potassium dihydrogen phosphate

Chemical forms of ^{32}P		Time elapsed after irradiation (days)		
		7	14	26
		%	%	%
Phosphate		43.5±0.4	43.7±0.4	45.4±0.5
Phosphite (+hypophosphite)		13.9±0.3	13.2±0.3	13.1±0.3
Pyrophosphate		11.8±2.0	14.7±2.6	15.2±2.6
Higher polyphosphates	R_f 0.09	19.6±3.3	9.6±1.6	21.5±3.7
	Others	9.9±3.2	14.9±4.8	4.5±1.5

TABLE III. SZILARD-CHALMERS EFFECT IN AMMONIUM DIHYDROGEN PHOSPHATE

Chemical forms of ^{32}P	Time elapsed after irradiation (days)			
	Sample I	Sample II		
	0	5	7	17
	%	%	%	%
Phosphate	47.8±0.7	54.1±0.8	56.4±0.9	55.9±0.8
Phosphite (+hypophosphite)	13.1±0.6	7.1±0.3	6.2±0.3	6.5±0.3
Pyrophosphate	8.4±1.6	18.1±2.8	15.0±2.8	15.3±2.8
Higher polyphosphates (R_f 0.09	29.3±4.8	12.7±2.8	8.7±1.9	17.4±2.9
Higher polyphosphates Others		7.0±3.6	13.5±7.0	

TABLE IV. SZILARD-CHALMERS EFFECT IN $NaH_2PO_4 \cdot 2H_2O$

Chemical forms of ^{32}P	Time elapsed after irradiation (days)			
	4	6	8	10
	%	%	%	%
Phosphate	78.2±0.6	83.5±0.7	83.0±0.7	77.8±0.6
Phosphite (+hypophsphite)	2.4±0.1	—	—	—
Pyrophosphate	16.8±2.0	9.9±1.2	9.9±1.2	11.7±1.4
Higher polyphosphates	2.4±0.2	6.5±0.7	6.9±0.7	10.4±1.0

TABLE V. SZILARD-CHALMERS EFFECT IN $NaH_2PO_4 \cdot H_2O$

Chemical forms of ^{32}P	Time elapsed after irradiation (days)
	4
	%
Phosphate	78.6±1.3
Phosphite (+hypophosphite)	4.7±0.2
Pyrophosphate	8.6±1.9
Higher polyphosphates	7.9±1.0

TABLE VI. SZILARD-CHALMERS EFFECT IN NaH_2PO_4

Chemical forms of ^{32}P	Time elapsed after irradiation (days)			
	1	7	8	10
	%	%	%	%
Phosphate	21.2±0.8	28.6±1.0	23.4±0.8	27.1±1.0
Phosphite (+hypophosphite)	17.3±0.3	14.9±0.2	18.8±0.3	15.7±0.3
Pyrophosphate	25.9±5.5	20.7±4.4	25.2±5.4	24.6±5.3
Higher polyphosphates (R_f 0.09	19.1±3.2	35.9±0.6	32.4±0.5	31.7±5.5
Higher polyphosphates Others	15.8±8.2			

TABLE VII. SZILARD-CHALMERS EFFECT IN $(NH_4)_2HPO_4$

Chemical forms of ^{32}P	Time elapsed after irradiation (days)		
	5	7	17
	%	%	%
Phosphate	34.2±1.0	35.3±1.1	36.4±1.2
Phosphite (+hypophosphite)	22.6±0.3	25.1±0.4	23.8±0.4
Pyrophosphate	13.3±4.2	16.0±5.1	15.0±4.8
Higher polyphosphates	24.8±5.3	14.3±3.0	15.3±3.3

TABLE VIII. SZILARD-CHALMERS EFFECT IN $Na_2HPO_4 \cdot 12H_2O$

Chemical forms of ^{32}P	Time elapsed after irradiation (days)		
	4	7	9
	%	%	%
Phosphate	70.3±1.2	77.8±1.3	84.3±1.4
Phosphite (+hypophosphite)	—	—	—
Pyrophosphate	28.1±0.7	22.2±0.6	15.6±0.4
Higher polyphosphate	1.5±0.2	—	—

TABLE IX. SZILARD-CHALMERS EFFECT IN Na_2HPO_4

Chemical forms of ^{32}P	Time elapsed after irradiation (day)						
	1	2	3	7	8	9	10
	%	%	%	%	%	%	%
Phosphate	24.3±1.7	22.4±1.5	19.8±1.4	22.0±1.5	25.1±1.7	28.1±1.9	21.7±1.5
Phosphite (+hypophosphite)	20.2±0.4	20.7±0.4	24.3±0.5	21.7±0.4	21.3±0.4	21.2±0.4	23.7±0.5
Pyrophosphate	16.5±2.0	23.8±2.8	19.4±2.3	22.5±2.7	22.4±2.7	19.1±2.3	23.5±2.8
Higher polyphosphates	37.5±2.6	31.5±2.1	34.6±2.4	32.4±2.2	31.0±2.1	31.1±2.1	29.6±2.0

TABLE X. SZILARD-CHALMERS EFFECT IN $Na_3PO_4 \cdot 12H_2O$

Chemical forms of ^{32}P	Time elapsed after irradiation (days)				
	1	2	5	8	12
	%	%	%	%	%
Phosphate	45.8±1.1	45.2±1.1	53.4±1.3	58.8±1.5	57.6±1.4
Phosphite (+hypophosphite)	47.3±1.2	44.6±1.1	37.2±0.9	30.9±0.8	32.2±0.8
Pyrophosphate Higher polyphosphates	6.7±0.4	10.0±0.7	9.3±0.6	9.8±0.6	9.8±0.6

were not completely separated. Phosphate and phosphite fractions did not show remarkable change with standing time.

Ammonium Dihydrogen Phosphate. — Two samples were tested. Sample I was irradiated in Hole No. 16 (neutron flux: 0.51×10^{12}n/cm^2/sec.) for 1 hr. and Sample II was irradiated, in Hole No. 12 (neutron flux: 0.38×10^{12}n/cm^2/sec.) for 15 hr. The results are shown in Table III. The sum of the fractions of phosphate and phosphite in Table III is almost constant, 61~62%, and the sum of pyrophosphate and higher polyphosphates is 37~38% except for the result after 17 days for Sample II.

Sodium Dihydrogen Phosphates. — Hydrous and anhydrous salts were tested. The results were markedly different from each other.

i) *$NaH_2PO_4 \cdot 2H_2O$.*—The target was irradiated in the Hole No. 12 (neutron flux: 0.38 10^{12}n/cm^2/sec.) for 15 hr. The results are tabulated in Table IV. The data show some irregularities especially in the fractions of pyrophosphate and higher polyphosphates, but time dependency of the distribution seems to be small. The experiment was not done immediately after irradiation because of the formation of ^{24}Na (half-life: 15.0 hr.).

ii) *$NaH_2PO_4 \cdot H_2O$.*—The target was irradiated in Hole No. 15 (neutron flux: 0.22×10^{12}n/cm^2/sec.) for 15 hr. The result shown in Table V are similar to those for $NaH_2PO_4 \cdot 2H_2O$.

iii) *NaH_2PO_4.*—The anhydrous salt was irradiated in Hole No. 3 (neutron flux: 0.48×10^{12} n/cm^2/sec.) for 5 hr. The results shown in Table VI are different from those for the hydrous salts. The difference is as follows. 1) The retention for the anhydrous salt is smaller than those for the hydrous salts. 2) The sum of the pyrophosphate and higher polyphosphate fractions for the anhydrous salt is larger than those for the hydrous salts. 3) The phosphite fraction for the anhydrous salt is larger than that for the hydrous salts.

Diammonium Hydrogen Phosphate.—The target was irradiated in Hole No. 12 (neutron flux: 0.38×10^{12}n/cm^2/sec.) for 15 hr. The results are shown in Table VII.

The sum does not attain to 100% because of the presence of tailing between the spots of pyro- and orthophosphate. The time dependency of distribution seems to be small. Three peaks appear in the fractions of polyphosphates.

Disodium Hydrogen Phosphates. — Both hydrous and anhydrous salts were tested.

i) *$Na_2HPO_4 \cdot 12H_2O$.*—The target was irradiated in Hole No. 3 (neutron flux: 0.48×10^{12}n/cm^2/sec.) for 5 hr. The results shown in Table VIII are different from the data for $Na_2HPO_4 \cdot 2H_2O$ and $Na_2HPO_4 \cdot 5H_2O$ in Aten's experiments[5]. Phosphite or hypophosphite can not be detected in Table VIII, while a large percentage of phosphite (or hypophosphite) appeared for $Na_2HPO_4 \cdot 2H_2O$ and $Na_2HPO_4 \cdot 5H_2O$ in Aten's work. In the table, the percentage of phosphate slowly increases with standing time while the percentage of pyrophosphate slowly decreases. Apparently, this is likely to be hydrolysis of pyrophosphate in to phosphate.

ii) *Na_2HPO_4.*—The target was irradiated in Hole No. 3 (neutron flux: 0.48×10^{12}n/cm^2/sec.) for 5 hr. The results are listed in Table IX. These are somewhat different from those in Aten's[5] and Sellers's work[5].

The distribution shows similar tendencies as those for NaH_2PO_4 (Table VI). These results are markedly different from those for the hydrous salt. 1) The retention for the anhydrous salt is smaller than that for the hydrous salt. 2) Fraction of pyrophosphate and higher polyphosphates in the anhydrous salt is larger than that in the hydrous salt. 3) An appreciable fraction of phosphite appears in the anhydrous salt, while it does not appear in the hydrous salts.

Trisodium Phosphates.—Both hydrous and anhydrous salts were tested.

i) *$Na_3PO_4 \cdot 12H_2O$.*—The target was irradiated in Hole No. 3 (neutron flux: 0.48×10^{12}n/cm^2/sec.) for 5 hr. The results are listed in Table X.

Fractions of phosphate and phosphite show remarkable changes with standing time. In Fig. 2, these changes are shown. Phosphite is slowly converted into phosphate.

ii) *Na_3PO_4.*—The target was irradiated in Hole No. 3 (neutron flux: 0.48×10^{12}n/cm^2/sec.) for 5 hr. The results are shown in Table XI.

Changes of fractions of phosphate and phosphate are shown in Fig. 3. The difference between the results of the hydrous and of the anhydrous salts is as follows. 1) Time dependency is remarkable in the hydrous salt, while it is scarcely ever observed in the anhydrous salt. 2) Retention in the hydrous salt is greater than that in the anhydrous salt. 3) Fractions of pyrophosphate and higher polyphosphates for the anhydrous salts are larger than that those in the hydrous salt.

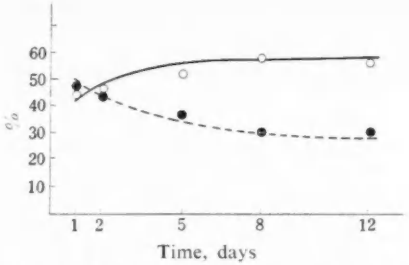

Fig. 2. Variation of percentages of ^{32}P components in $Na_3PO_4 \cdot 12H_2O$. (The phosphate content in % is shown by the solid line and the phosphite (+hypophosphite) content in % is shown by the broken line).

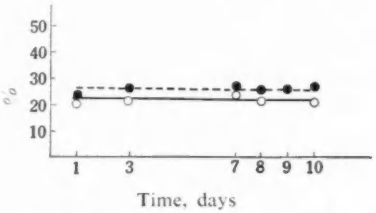

Fig. 3. Variation of percentages of ^{32}P components in Na_3PO_4. (The phosphate content in % is shown by solid line and the phosphite (+hypophosphite) content in shown by the broken line).

Zinc Phosphate.—The target was irradiated in Hole No. 3 (neutron flux: 0.48×10^{12}n/cm^2/sec.) for 5 hr. The results are shown in Table XII. The results were similar to those for Na_3PO_4 (anhydrous).

Sodium Phosphite ($Na_2HPO_3 \cdot 5H_2O$). — The target was irradiated in Hole No. 3 (neutron flux: 0.48×10^{12}n/cm^2/sec.) for 5 hr. The results are tabulated in Table XIII.

TABLE XI. SZILARD-CHALMER EFFECT IN Na_3PO_4

Chemical forms of ^{32}P	Time elapsed after irradiation (days)					
	1	3	7	8	9	10
	%	%	%	%	%	%
Phosphate	20.7±0.5	22.1±0.6	23.5±0.6	22.2±0.6	25.9±0.7	28.4±0.7
Phosphite (+hypophosphite	24.2±0.6	26.3±0.6	27.3±0.6	25.9±0.6	25.7±0.6	23.2±0.6
Pyrophosphate	18.3±5.0	47.0±1.0	48.2±1.0	16.8±4.8	18.2±5.0	19.4±5.2
Higher polyphosphates	35.1±7.7			32.2±7.0	28.8±6.3	28.4±6.2

TABLE XII. SZILARD-CHALMERS EFFECT IN $Zn_3(PO_4)_2$

Chemical forms of ^{32}P	Time elapsed after irradiation (days)	
	1	7
	%	%
Phosphate	29.6±1.1	34.5±1.3
Phophate (hypophosphite)	36.2±1.4	35.7±1.2
Pyrophosphite	9.3±0.9	28.8±0.6
Higher polyphosphates	24.8±2.0	

TABLE XIII. SZILARD-CHALMERS EFFECT IN $Na_2HPO_3 \cdot 5H_2O$

Chemical forms of ^{32}P	Time elapsed after irradiation (days)			
	2	5	12	15
	%	%	%	%
Phosphate	4.5±0.1	4.3±0.1	4.0±0.1	2.9±0.1
Phosphite (+hypophosphite)	77.2±8.3	76.0±8.2	77.9±8.4	82.0±8.9
Pyrophosphate	9.6±0.9	7.6±0.7	5.4±0.5	4.8±0.5
Higher polyphosphates	7.6±0.7	10.9±1.0	7.6±0.7	7.5±0.7

TABLE XIV. SZILARD-CHALMERS EFFECT IN $Na_4P_2O_7 \cdot 10H_2O$

Chemical forms of ^{32}P	Time elapsed after irradiation (days)				
	2	5	12	15	22
	%	%	%	%	%
Phosphate	47.9±2.4	44.2±2.2	51.4±2.5	53.9±2.7	50.2±2.5
Phosphite (−hypophosphite)	—	—	—	—	—
Pyrophosphate	45.3±2.3	43.4±2.2	35.5±1.8	34.5±1.8	38.1±1.9
Higher polyposphates	7.1±0.5	12.1±0.9	12.8±0.9	11.0±0.8	11.6±0.8

TABLE XV. SZILARD-CHALMERS EFFECT IN $Na_4P_2O_7$

Chemical forms of ^{32}P	Time elapsed after irradiation (days)
	4
	%
Phosphate	9.4±1.6
Phosphite (+hypophosphite)	24.8±0.9
Pyrophosphate	36.2±4.2
Higher polyphosphates	26.5±2.3

Several components also appear in the chromatogram, but the major component is the parent substance. Pyrophosphate and higher polyphosphates are detected in appreciable quantities. Changes by standing time are not great.

Sodium Pyrophosphates.—Both hydrous and anhydrous salts were tested.

i) *$Na_4P_2O_7 \cdot 10H_2O$.*—The target was irradiated in Hole No. 3 (neutron flux: 0.48×10^{12} n/cm^2/sec.) for 5 hr. The results are listed in Table XIV.

The distribution slightly changed by standing time.

ii) *$Na_4P_2O_7$.*—The anhydrous salt was irradiated in Hole No. 12 (neutron flux: 0.38×10^{12} n/cm^2/sec.) for 15 hr. The result is shown in Table XV.

There are great differences between the results of the hydrous and of the anhydrous salt. 1) The phosphate fraction in the anhydrous salt is much smaller than that in the hydrous salt. 2) The phosphite fraction is not detected for the hydrous salt, while it is more than 20% for the anhydrous salt.

Discussion

On the study on the Szilard-Chalmers effect, the exchange reaction between the separated atoms and parent substance is an important factor. If this exchange reaction occurred rapidly, we could not observe the Szilard-Chalmers effect. Several exchange reactions of phosphorus acids have been investigated so far. No isotopic exchange of phosphorus was

detected in the systems: $H_3PO_4+H_3PO_2$[9,10], $H_3PO_4+H_3PO_3$[10,11], $H_3PO_4+(HPO_3)_3$[12], $(NaPO_3)_3+(NaPO_3)_6$ and $(NaPO_3)_3$[13], $NaH_2PO_4+(NaPO_3)_6$[13]. Therefore, the effect of the exchange reaction between the parent substance and the daughter species can be ignored in the present paper. The phosphite fraction seems to become larger in the order of the targets of phosphoric acid, primary, secondary and tertiary phosphate. But this is not applicable to the hydrous salts.

Ammonium chromate[14] and iodate[15] show a much lower retention value in the Szilard-Chalmers effect than other alkali chromates and iodates do. Namely, the yield of the reduced form for the ammonium salts is much higher than that for other alkali salts. Therefore, Harbottle et al.[16] suggested that the ammonium ion may act as a reducing agent in the hot zone. However, in the present case the yield of the reduced forms for ammonium phosphates is not markedly higher than that for the corresponding alkali phosphates. Perhaps the ammonium ion does not act as a reducing agent to phosphate in the hot zone. This may be attributed to the difference in oxidation potential of phosphate and chromate or iodate to their reduced forms.

Remarkable differences are present between the Szilard-Chalmers effects of anhydrous and hydrous phosphates. Retention in the Szilard-Chalmers effect of the hydrous salt is generally greater than that of the anhydrous salt. In the cases of $NaH_2PO_4\cdot 2H_2O$, $NaH_2PO_4\cdot H_2O$ and $Na_2HPO_4\cdot 12H_2O$, the fraction of phosphite (or hypophosphite) is smaller than that in the anhydrous salts. Similar effects are observed in the cases of hydrous and anhydrous sodium pyrophosphates. The water molecule seems to act as an oxidizing agent for these salts. However, in the case of $Na_3PO_4\cdot 12H_2O$, the fraction of phosphite (+hypophosphite) is larger than that for the anhydrous salt. This seems to be inconsistent with the fact that the water molecule apparently acts as an oxidizing agent in the former cases, but the reason is not yet clear. Usually phosphite (or hypophosphite) changes slowly into phosphate by standing in the case of the hydrous salt, while it scarcely changes in the case of the anhydrous salt. This time dependency may be attributable to the formation of any oxidizing agent in the presence of the water molecule. Phosphite (or hypophoshite) may react slowly with this oxidizing agent and change into phosphate. Fractions of pyrophosphate and higher polyphosphates are smaller for the hydrous salt than those of the anhydrous salt. This fact may be interpreted by the dilution effect (or any other hindrance effect) of the water molecule on the condensation of phosphate in the solid state.

Formation of pyrophosphate and higher polyphosphates occurs in all phosphorus acids and their salts which have been tested. The presence of higher polyphosphates has not been pointed out clear by so far. The condensation reaction of phosphate to condensed polyphosphates usually occurs at a high temperature. For example, orthophosphoric acid is converted into pyrophosphoric acid by heating at 250°C. Therefore, the experiments may suggest that the high temperature reactions play important roles in the present cases. Really, at the event of the recoil a large amount of heat is liberated, and it is expected that the neighbor of the recoil atom is raised up to a high temperature[17]. According to the calculation based on the theory of Hatbottle et al.[17], the hot zone in an ionic crystal includes about 1000 atoms at 1000°K, and about 2000 atoms at 500°K, provided that the recoil energy is about 300 eV.

The spot at the R_f value of 0.09 appears only in the primary phosphates. This is likely to correspond to polymetaphosphate. This may be produced by the following reaction:

$$n\mathrm{MH_2PO_4} \rightarrow (\mathrm{MPO_3})_n + n\mathrm{H_2O}.$$

In the cases of the molecular and ionic crystals which are unstable to heat, the mechanism of the thermal reaction in the hot-zone is likely to be very important. This localized thermal reaction or high temperature reaction may be necessary to explain some complicated phenomena in the Szilard-Chalmers effect.

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Natural Furan Derivatives. V[1]. *The Number of Double Bonds in Obacunone*

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(Received July 21, 1960)

Obacunone ($C_{26}H_{30}O_7$) is known as the bitter principle contained in the plants of the *Rutaceae* family, together with limonin[2] and nomilin[3]. It has been studied by many investigators[3-6] since the beginning of this century. Casimirolid, isolated from *Casimiroa edulis* Lave et Lex, was recently proved to be identical with obacunone[7-10].

Studies made to date have revealed the presence of one ketone group and two lactone groups, one being opened reversibly and the other being an α,β-unsaturated lactone group which suffers irreversible fission. Of the remaining two oxygen atoms, one has been proved by Kubota and Tokoroyama[11] to be present in β-substituted furan ring and the other is considered to be present as an oxide bond from its inert nature.

Dean and Geissman[6] concluded from spectroscopic studies on obacunone and nomilin (acetoxydihydroobacunone with an acetoxyl group in the β-position of the unsaturated lactone group in obacunone)[3] and from the complicated behavior of these two compounds toward catalytic reduction* that obacunone had another double bond besides the three in the furan ring and the α,β-unsaturated lactone group, and that it is a monocarbocyclic compound. The present paper presents evidences that obacunone possesses only three double bonds.

Obacunone (I) easily undergoes the addition of one mole of hydrogen chloride to form obacunone hydrochloride (II)[6]. Since this compound does not show the characteristics of an α,β-unsaturated lactone and easily regenerates obacunone on being heated with pyridine, it is clear that the addition of hydrogen chloride has taken place at the double bond in the α,β-unsaturated lactone group[6].

Ozonolysis of obacunone hydrochloride at room temperature affords an acid, $C_{23}H_{35}O_8\cdot HCl$, by losing three carbon atoms. The acid has been named etioobacunoic acid hydrochloride (III) which is characterized as its methyl ester (IV), $C_{24}H_{39}O_8\cdot HCl$. III and IV do not show infrared absorption characteristics of the furan ring at 3.18, 6.66 and 11.42 μ[12]. Treatment of III with pyridine results in dehydrochlorination and a dilactone-carboxylic acid, etioobacunoic acid (V), $C_{23}H_{28}O_8$, is formed. Etioobacunoic acid shows the absorption of a double bond conjugated with a carboxyl group at 6.18 μ and an absorption maximum at 214.5 mμ (ε 11,500) indicating that the α,β-unsaturated lactone system has been regenrated as in the case of the conversion of obacunone hydrochloride to obacunone. It follows, therefore, that the change of obacunone to etioobacunoic acid may be indicated as follows:

$$(C_{22}H_{27}O_6)\!\!\begin{array}{|c|}\hline \\ O \\ \hline\end{array} \rightarrow (C_{22}H_{27}O_6)\text{-}CO_2H$$

I V

Hydrolysis of obacunone results in the irreversible fission of the unsaturated lactone ring and an unsaturated hydroxy acid, obacunoic acid (VIII), is formed[5]. Mild hydrolysis of etioobacunoic acid (V) also gives an unsaturated hydroxy-dicarboxylic acid $C_{23}H_{30}O_9$, which has been named etioobacunone-dicarboxylic acid (IX) and shows absorptions at 2.96 (hydroxyl) and 6.18 μ (conjugated double bond). Careful methylation of IX with diazomethane affords a dimethyl ester (X) corresponding to methyl obacunoate[5].

Methyl etioobacunoate hydrochloride (IV) gives no coloration with tetranitromethane.

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* Catalytic reduction of obacunone and its allied compounds will be reported in subsequent papers.
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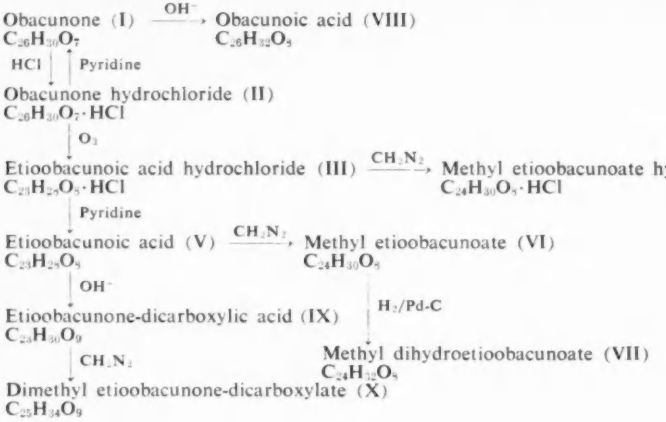

Also its ultraviolet absorptions are weak in intensity, being end absorptions at 207 mμ (ε 520) and at 210 mμ (ε 400). If acid III should retain a double bond of poor reactivity with ozone and with tetranitromethane and thus a double bond of a tetrasubstituted ethylene, compound IV should show an absorption maximum of strong intensity of several thousands in ε at around 205 mμ[13]. Catalytic reduction of methyl etioobacunoate (VI) results in absorption of one mole of hydrogen to form methyl dihydroetioobacunoate (VII), which does not color with tetranitromethane and shows an end absorption of low intensity at 205 mμ (ε 850). Consequently, it follows that IV and VII are completely saturated and therefore it is concluded that obacunone possesses three double bonds, two in the furan ring and one in the α,β-unsaturated lactone group, and that it possesses a bicarbocyclic ring.

Experimental

Etioobacunoic Acid Hydrochloride (III).—Obacunone hydrochloride (2.0 g.), which was prepared according to the method of Dean and Geissman[6], was dissolved in methylene chloride (50 ml.) and ozonized until the solution was saturated with ozone. The mixture was poured into water (50 ml.) and allowed to stand for several days with occasional swirling. The separated crystals were filtered and recrystallized from acetone-water as needles (1.1 g.), m. p. 238~240°C (decomp.). Infrared absorption (Nujol): 3.6~4.1 (carboxylic group), 5.74 (lactone goups), 5.96~6.00 μ (ketone and carboxylic groups).

Found: C, 58.61; H, 6.43. Calcd. for $C_{25}H_{29}O_5Cl$: C, 58.91; H, 6.23%.

Methyl Etioobacunoate Hydrochloride (IV).—A solution of etioobacunoic acid hydrochloride in acetone was methylated with an ether solution of diazomethane. Repeated recrystallization of the product from acetone-water gave needles, m. p. 202°C (decomp.). Infrared absorption (Nujol): 5.74~5.77 (lactone and ester groups), 5.83 μ (ketone group).

Found: C, 59.53; H, 6.61. Calcd. for $C_{26}H_{31}O_5Cl$: C, 59.68; H, 6.47%.

Etioobacunoic Acid (V).—Etioobacunoic acid hydrochlorid (150 mg.) was dissolved in pyridine (2 ml.) and the solution refluxed for 1 hr. After removal of the solvent under reduced pressure, the residue was dissolved in water and the solution was acidified with dilute sulfuric acid. Recrystallization of the resulting precipitates (132 mg.) from acetone-water gave needles, m. p. 236°C (decomp.). Infrared absorption (Nujol): 3.3~4.1 (carboxylic group), 5.74 (lactone groups), 6.00~6.05 (carboxylic group, ketone and α,β-unsaturated lactone group), 6.18 μ (conjugated double bond).

Found: C, 63.76; H, 6.80. Calcd. for $C_{25}H_{28}O_5$: C, 63.88; H, 6.53%.

Neutralization equivalent: 423 (Calcd. value 432.5). Saponification equivalent: 150 (Calcd. value: 144.2).

Methyl Etioobacunoate (VI).—A solution of etioobacunoic acid in a mixture of acetone and methanol was methylated with an excess of diazomethane in ether. Recrystallization of the product from acetone-water gave needles, m. p. 275~277°C, in a practically quantitative yield. Infrared absorption (Nujol): 5.69 (lactone group), 5.75 (ester group), 5.89~5.92 μ (ketone and α,β-unsaturated lactone groups).

Found: C, 64.52; H, 6.67. Calcd. for $C_{24}H_{30}O_5$: C, 64.56; H, 6.77%.

Methyl Dihydroetioobacunoate (VII).—Methyl etioobacunoate (500 mg.) dissolved in a mixture of ethyl acetate (25 ml.) and dioxane (10 ml.) was shaken with hydrogen at 31°C in the presence of 10% palladium-charcoal (100 mg.). Absorption of 1 mol. (31 ml.) of hydrogen was completeted in 4⅛ hr. After filtration of the catalyst, the solvent was evaporated under reduced pressure. Recrystallization of the residue from acetone-water or from ethanol gave prisms, m. p. 236~237°C. Infrared

13) P. Blauden, H. B. Henbest and G. W. Wood, *J. Chem. Soc.*, 1952, 2737.

absorption (Nujol): 5.72~5.88 μ (lactones, ester and ketone groups). Ultraviolet absorption: λ_{205}^{EtOH}, ε 850; λ_{210}^{EtOH}, ε 525.

Found: C, 63.81; H, 7.50. Calcd. for $C_{24}H_{32}O_5$: C, 64.27; H, 7.19%.

Saponification equivalent: 146 (Calcd. value: 149).

The dihydroester (VII) was also obtained by the hydrogenation of methyl etioobacunoate in the presence of palladium-alumina[14] in dioxane.

Etioobacunone-Dicarboxylic Acid (IX).—Etioobacunoic acid (2 g.) was dissolved in 1 N potassium hydroxide (20 ml.) and the solution heated below 80°C for 1 hr. After cooling the solution was acidified with 1 N hydrochloric acid (Congo Red). The separated crystals were collected and recrystallized twice from dilute methanol as needles (0.9 g.), m. p. 192~193°C (decomp.). Infrared absorption (Nujol): 2.97 (hydroxyl group), 3.07 (hydroxyl group), 5.74 (lactone group), 5.84 (ketone and carboxylic groups), 6.18 μ (conjugated double bonds). Ultraviolet absorption: λ_{205}^{EtOH} ε 5,500; λ_{210}^{EtOH}, ε 5,500.

Found: C, 61.24; H, 6.89. Calcd. for $C_{25}H_{30}O_6$: C, 61.32; H, 6.71%.

Dimethyl Etioobacunone-dicarboxylate (X).—To a solution of etioobacunone-dicarboxylic acid (IX) in methanol was added an ethereal solution of diazomethane in an amount less than the theoretical. Immediately after the addition of diazomethane, the solvent evaporated under reduced pressure. The residue was dissolved in chloroform and the solution was shaken with aqueous bicarbonate to remove an acidic material. The chloroform layer was washed with water, dried and evaporated. Recrystallization of the residue from acetone-water, then from ethanol, gave needles, m. p. 177~178°C. Infrared absorption (Nujol): 2.81 (hydroxyl group), 5.73 (lactone and ester groups), 5.82 (α, β-unsaturated ester group), 5.88 (ketone group), 6.15 μ (conjugated double bond).

Found: C, 62.61; H, 7.43. Calcd. for $C_{25}H_{34}O_6$: C, 62.75; H, 7.16%.

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Summary

Obacunone has only three double bonds in total, two in its furan ring and one in its α, β-unsaturated lactone group and, therefore, it possesses a bicarbocyclic ring.

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The Use of Radioactive Fission Product Rare Gases for the Study of the Change in Crystal Structure

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(Received July 14, 1960)

In our previous paper[1], the possible correlation between released fission rare gas which was captured in a sample of hematite by its recoil energy and the crystal structure change was reported, and the use of radioactive fission product rare gas for the emanation method in place of radon was proposed. In our present work, the experiment was carried out more extensively using the high temperature X-ray diffraction method to confirm the correlation. The usefullness of this emanation method using radioactive fission rare gas in place of radon for the studies in the field of physical chemistry is also discussed.

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Experimental

Usable Nuclides in Fission Product Rare Gases for the Emanation Method.—A major fraction of Uranium-235 thermal fission products consist of gaseous materials and the sum of independent and primary cumulative yields of all gaseous fission products, including iodine, bromine, xenon and krypton, amount to 52.3%. Of this value 55.3%, or a yield of 28.9%, is attributed to xenon and krypton.

Referring to a table of isotopes[2], krypton-85m, xenon-135 and xenon-133 have considerably long half-lives and large fission yields. To investigate the interference of the precursor and the radioactivity of the other nuclides, the changes of the radioactivity of the krypton-85m, xenon-135 and xenon-133 after two hours' irradiation with time are measured and these changes are plotted in Fig. 1. In these experiments, a closed polyethylene sheet containing 20 mg. of uranium dioxide was irradiated

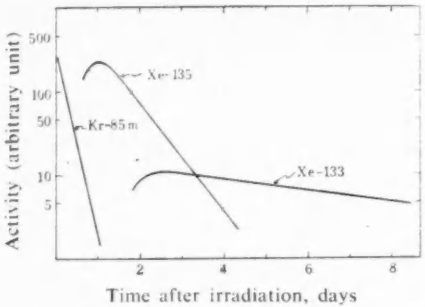

Fig. 1. Change of the radioactivities of the fission product krypton and xenon with time after two hour irradiation.

by thermal neutrons (flux, $\sim 5 \times 10^{11}$ n/cm^2 sec.) for two hours. The sample is placed in a small flask after each cooling period and the sheet is broken, and the uranium dioxide is dissolved in concentrated nitric acid. Helium is made to flow through the flask, a trap is cooled by dry ice (for iodine) and a charcoal trap is cooled by liquid nitrogen (for xenon and krypton) during treatments and for ten minutes after the uranium has been dissolved. The radioactivities of the krypton and xenon trapped in charcol are measured by a multi-channel gamma ray spectrometer. Their gamma-ray spectra are shown in Fig. 2. The cooling periods to minimize the interference of precursor and radioactitvity of the other nuclides are found to be 1.5 and 4 days for xenon-135 and xenon-133, respectively. The use of one of these nuclides depends on the nature of the sample and the function of the measuring instrument, and the cooling period is therefore determined by the nuclide thus selected.

Preparation of the Heating Curve and X-ray Diffraction Measurement. — In the emanation method, the samples containing radioactive rare gases were heated at a constant rate and the radioactivity of the escaping rare gases was measured (heating curves), or the samples were heated at various temperatures and kept at these temperatures while the changes in escaped radioactivity with time were followed (isothermal curves). In the present

TABLE 1. THE HEMATITE SAMPLES AND THEIR PREPARATION METHODS

Sample No.	Chemical form	Preparation method
1	α-Fe_2O_3	Dehydration of α-FeO·OH at 250°C
2	α-Fe_2O_3	Dehydration of α-FeO·OH at 300°C
3	α-Fe_2O_3	Thermal decomposition of $FeSO_4 \cdot 7H_2O$ at 780°C
4	γ-Fe_2O_3	Oxidation of Fe_3O_4 at 250°C
5	γ-Fe_2O_3	Pure γ-Fe_2O_3

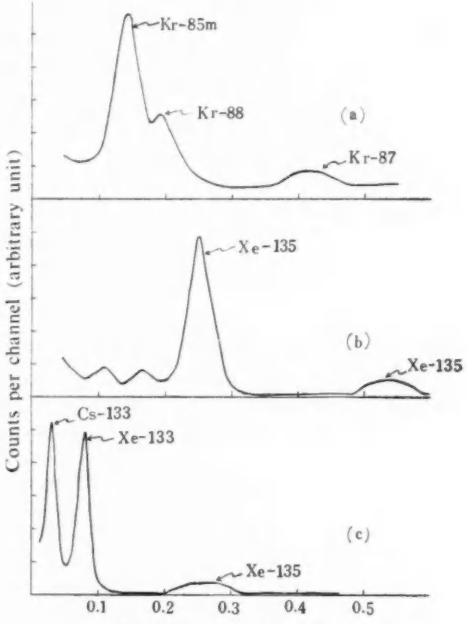

Fig. 2. Gamma-ray spectra of the fission product rare gases.
(a) 2 hr. irradiation and 8 hr. cooling.
(b) 2 hr. irradiation and 1.5 day colling.
(c) 2 hr. irradiation and 5 day cooling.

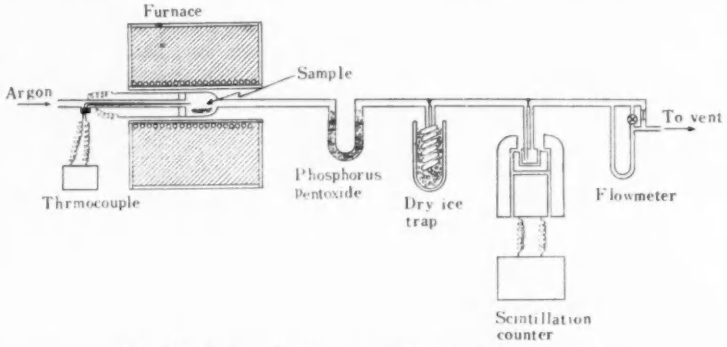

Fig. 3. Schematic diagram of the heating apparatus.

work, the crystal structure change of γ-hematite to α-hematite is studied by the heating curve. An X-ray diffraction method is also employed to identify the crystal structures. The samples of hematites to be examined are shown in Table I.

Two hundred milligrams of thin film of formvar, in a small size, containing uranium dioxide of which the weight ratio to formvar is 1 : 5 was mixed with 500 mg. of hematite and irradiated by thermal neutron flux $\sim 5 \times 10^{11}$ n/cm² sec. for 2 hr. in an experimental hole of JRR-1 reactor. Then the fission recoil energy enables the fission products to be caught by the surrounding solid powder through the film[4-6]. After 1.5 days' cooling ethyl alcohol was added to the sample and the solid powder retaining fission products was separated by a wire gauze and filter paper and was dried. The solid powder was placed in a quartz boat in a quartz tube which was connected to a phosphorus pentoxide drying tube, a dry ice trap for radioactive iodine, a counting cell inserted into an NaI scintillation crystal well of a γ-ray spectrometer and a flow rate meter, in the order mentioned. The schematic diagram of the apparatus is shown in Fig. 3. Solid powder was heated by a furnace at a rate 5 °C/min. in a current of argon (100 ml. per min.). The radioactive xenon-135 escaping from hematite was carried by argon and the radioactivity was measured with the scintillation counter. Plots of the radioactivity of xenon-135 escaped from the sample versus temperature are shown in Fig. 4.

The correlations between the observed peaks in the heating curves and the crystal structure changes were studied by the high temperature X-ray diffraction method at temperatures below and over the temperatures where the peaks appear. γ-Hematite samples (Nos. 4 and 5) were investigated by the continuous recording method, by the use of the peaks (220) of γ-hematite and (104) of α-hematite. The charts are shown in Figs. 5 and 6.

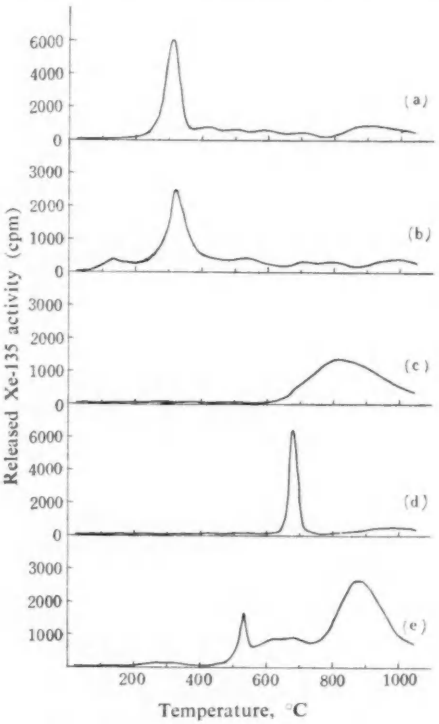

Fig. 4. Heating curves (5°C/min.) of hematite samples.
(a) No. 1 α-hematite sample.
(b) No. 2 α-hematite sample.
(c) No. 3 α-hematite sample.
(d) No. 4 γ-hematite sample.
(e) No. 5 γ-hematite sample.

4) R. Wolfgang, *J. Inorg. Nucl. Chem.*, **2**, 180 (1956).
5) R. Henry and C. Herczeg, UNESCO/NS/RIC/14 (1957).
6) T. Nakai and S. Yajima, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **79**, 1267 (1958).

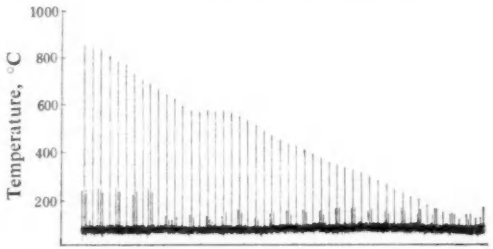

Fig. 5. Continuous recording chart of high temperature X-ray diffraction of No. 4 γ-hematite sample. Successive vertical lines indicate temperature.

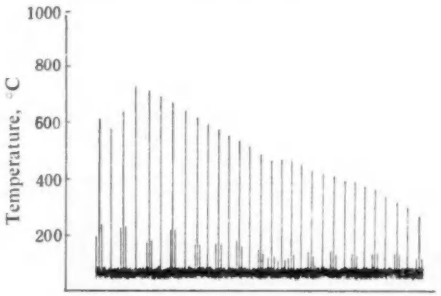

Fig. 6. Continuous recording chart of high temperature X-ray diffraction of No. 5 γ-hematite sample. Successive vertical lines indicate temperature.

Results and Discussion

The peaks in the heating curves of Nos. 1 and 2 samples are considered to be related to the dehydration of FeO·OH, although the X-ray diffraction chart shows that the No. 2 sample is in α-hematite form at room temperature. In the heating curve of No. 3 sample, no sharp peak is observed because no change

in structure takes place. The slow ascendant of the curve probably shows that the xenon trapped in the dislocation of the crystal is released. The samples of Nos. 4 and 5 are identified to be γ-hematite at room temperature by the X-ray diffraction method but their heating curves of Fig. 4 are considerably different from each other. The charts of the continuous recording method of Figs. 5 and 6 show that peaks at 680°C and 530°C are the temperatures of the crystal structure change of γ-hematite of samples Nos. 4 and 5 to α-hematite, respectively. The difference of their crystal structures might be investigated in detail by other methods, e.g., electron diffraction method.

The heating curves of the emanation method will suggest the temperature at which the crystal-structure change, dehydration and decomposition occur and also the detailed difference of the crystal structure for which the X-ray diffraction method does not give sufficient informaton. The heating curves may also suggest the possible existence of the dislocation of the crystal.

On the basis of the following reasons, the proposed method will promise a future development in various fields of the study.

1) This method will be applicable to many solids because the samples are prepared without chemical treatments.

(2) Different radioactive rare gases can be used at the same time. For example, prior to the reaction, if different nuclides of radioactive rare gas were retained in the reactants, the more detailed knowledge of the reaction between solids would be obtained.

3) When most of the rare gas is released at the first peak, it is possible to investigate the emanation at the higher temperature above the peak by means of the decay products of the precursor.

The radiation damage of the crystal will be negligible because the radioactivity of the fission rare gases is detected very sensitively and the sample does not require so much irradiation, as radiation damage occurs. The fission products captured in the solid will be also negligible as impurities.

The proposed method will be useful for the studies of crystal-structure change, reaction between solids and other problems of physical chemistry when the X-ray diffraction method and electron diffraction method are employed at the same time.

The authors wish to thank Professor S. Kachi of Kyoto Uuiversity for invaluable suggestions to this work and also for providing the hematite samples.

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SHORT COMMUNICATIONS

Rapid Separation of Nuclides in Fission Products and their Determinations by Focussing Chromatographic Method

By Mutsuaki SHINAGAWA, Yoshiyuki KISO and Akira OYOSHI

(Received October 14, 1960)

Although many procedures such as ion exchange, extraction, paper chromatographic and precipitation methods etc. have been applied to the separation of nuclides in fission products, the present focussing chromatographic method has been proved to be more rapid and convenient for their determinations comparing with other methods mentioned above.

The apparatus and its manipulation were the same as in previous paper[1]. As the complexing agent of cathodic solution, 0.1 M citric, oxalic, malonic, malic, maleic, lactic, succinic and tartaric acid, 0.05 M sodium triphosphate, 0.01 M EDTA and NTA were used and hydrochloric acid was used as cathodic solution in the present experiment.

The separation of several kinds of nuclide in fission products (imported from U. S. A.) were possible in a few minutes by the adjustment of pH value between both solutions of hydrochloric acid and complexing agent under suitable conditions of initial dipped width of sample solution (1~3 cm.) and applied voltage (750~1000 V./20 cm. of strip length). The autoradiographic method was used to decide the position of separated lines. Identification of nuclides was carried out by measuring their half-lives and energies.

Autoradiogram exemplified in Fig. 1, shows the situation of separation obtained by hydrochloric acid-citric acid system. Fig. 2 shows the general view of the separated patterns obtained with several complexing agents.

Separated lines of ^{137}Cs and ^{95}Zr in fission products were formed with the complexing agent without mutual contaminations. Quantitative determinations of ^{137}Cs and ^{95}Zr proved

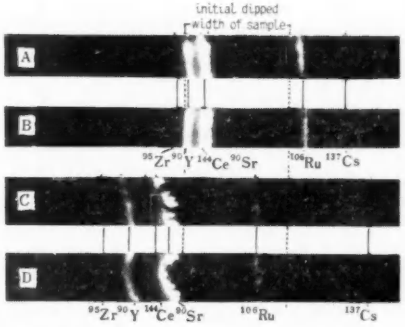

Fig. 1. Autoradiogram of separated lines of nuclides in fission product.
Complexing agent: 0.5 M citric acid (pH 4.5), hydrochloric acid: pH 1.5, initial dipped width of sample: 3 cm., sample volume: 0.05 ml. at A and B, 0.1 ml. at C and D, applied voltage: 1000 V./20 cm., duration time of applied voltage: 5 min. at A and B, 10 min. at C and D, autoradiographic exposure time: 2 hr., X-ray film: Fuji medical, 25 cm. × 30 cm., paper strip: Toyo Roshi No. 50.

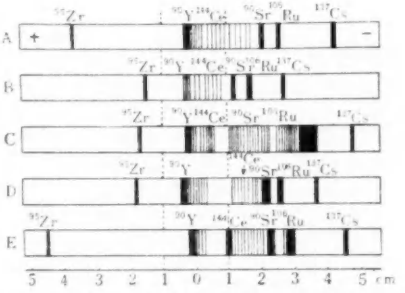

Fig. 2. General view of the separated pattern obtained with several complexing agents.
A: 0.1 M malonic acid, B: 0.1 M succinic acid, C: 0.1 M lactic acid, D: 0.1 M malic acid, E: 0.1 M maleic acid.
Anodic solution: 0.05 N hydrochloric acid and sodium chloride, cathodic solution: pH 7.0.
Applied voltage: 700 V./20 cm., duration time of applied voltage: 15 min., initial dipped width of sample: 2 cm., autoradiographic exposure time: 24 hr., paper strip: Toyo Roshi No. 50, X-ray film: Fuji medical, 25 cm. × 30 cm.

1) *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), in press; (Presented at the 8th Annual Meeting of the Japan Society for Analytical Chemistry, Okayama, Oct., 1959).

to be effective by measuring γ-activity of their separated lines cut from the paper strip. The mean deviation rate of reproducibility of radioactivity obtained and recovery were found within $\pm 5\%$ and $95 \pm 5\%$ respectively, from the result of blank test using the standard sample solution prepared by mixing with known amounts of ^{95}Zr (^{95}Nb), ^{144}Ce (^{144}Pr), ^{90}Sr (^{90}Y) and ^{106}Ru (^{106}Rh). Even when the closeness or overlapping of separated lines of ^{90}Y and ^{144}Ce, or ^{90}Sr and ^{106}Ru, the determinations of ^{144}Ce and ^{106}Ru by γ counting were feasible with an accuracy of the same order as ^{137}Cs and ^{95}Zr, because ^{90}Y and ^{90}Sr have no γ-activity.

The proposed method is considered to be a new rapid and simple method for analysis of product; i.e. fall-out analysis, burn-up determination of nuclear fuels, etc.

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On the Constitution of Sulfo-Aluminous Clinker

By Nobue FUKUDA

(Received October 26, 1960)

According to Lafuma[1], sulfo-aluminous clinker is produced by burning the mixture of gypsum, bauxite, and calcium carbonate, and is used as an expansive agent for the manufacture of expansive cement.

He succeeded in identifying the minerals, free anhydrous calcium sulfate, calcium aluminates particularly $5CaO \cdot 3Al_2O_3$, and γ $2CaO \cdot SiO_2$ in the clinker, but he could not confirm the ternary compound, calcium-sulfo-aluminate.

In the course of previous studies[2] on the system CaO-Al_2O_3-$CaSO_4$, the author could conclusively establish the existence of a ternary compound of the composition $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ which gave the X-ray diffraction data as shown in Table I.

With the opinion that this ternary compound may be expected to exist in sulfo-aluminous clinker the author has carried out the following experiments.

1) Heating the mixture of bauxite, lime, and gypsum for 30 min. at 1350°C the clinker was prepared, which was similar in appearance as described by Lafuma.

2) A series of sulfo-aluminous clinkers with the mole ratios of Al_2O_3/SO_3, 8.2, 6.0, 3.5, 2.0 and 0.8, respectively, were prepared by heating the batches containing different amounts of gypsum under the same conditions as above.

The samples 1 and 2 were identified by the determination of their chemical composition, X-ray diffraction patterns (powder method), and quantitative X-ray analysis using standard substances.

The X-ray data and chemical composition of sample 1, and the chemical composition of sample 2 are given in Tables II, III and IV.

The results are summarized as follows:

a) The existence of $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ as the main constituent in sulfo-alminous clinker has definitely been established.

b) The amount of this ternary compound in clinkers estimated from the content of Al_2O_3 or $CaSO_4$ determined by the chemical

TABLE I. X-RAY DIFFRACTION DATA OF $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$

d, Å	3.75	3.24	2.91	2.65	2.46	2.30	2.17	1.62	1.58
Int.	100	7	6	29	7	4	24	7	4

TABLE II. X-RAY DIFFRACTION DATA OF CLINKER

d, Å	3.75	3.49	3.25	2.91	2.85	2.79	2.71	2.65	2.46	2.34	2.17	1.63
Int.	100	59	10	—	12	20	4	30	11	—	37	13

TABLE III. CHEMICAL ANALYSIS OF CLINKER 1 (wt. %)

SiO_2	7.08	TiO_2	0.38	CaO	42.64
Al_2O_3	21.82	Fe_2O_3	5.38	SO_3	22.26

Content of $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$; Calcd. 43.50. By X-ray analysis. 39.20.

1) H. Lafuma, *Proc. of the 3rd. International Symposium on the Chemistry of Cement, London* (1952).

2) N. Fukuda, submitted to *J. Chem. Soc. Japan, Ind. Chem. Sec.*, (*Kogyo Kagaku Zasshi*).

TABLE IV. CHEMICAL ANALYSIS OF CLINKERS 2 (WT. %)

Al_2O_3	35.30	34.27	30.84	28.41	21.80
SO_3	3.36	4.52	7.02	10.98	21.12
Al_2O_3/SO_3 mole ratio	8.2	6.0	3.5	2.0	0.8
$3CaO \cdot 3Al_2O_3\ CaSO_4$					
Calcd.	25.64	34.18	53.49	56.72	43.48
By X-ray analysis.	27.65	33.80	57.00	56.00	41.05

analysis is in fairly good agreement with the results of direct measurements by quantitative X-ray analysis. The author, furthermore, has found that the amount of this compound is in equivalent with Al_2O_3-content when $Al_2O_3/SO_3<3$, and with $CaSO_4$-content when $Al_2O_3/>SO_3>3$.

c) As for the other constituents the existence of free anhydrous calcium sulfate was distinctly observed, while that of β $2CaO \cdot SiO_2$ was not so clear.

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Einwirkung von Thionylchlorid auf Diarylāthinylcarbinolen

Von Tsuneyuki NAGASE

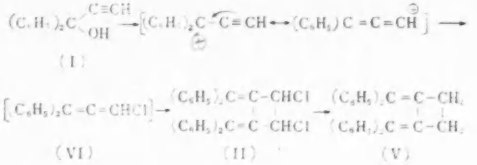
(Eingegangen am 22. Oktober, 1960)

Diphenyläthinylcarbinol (I) ergab bei der Einwirkung von Thionylchlorid in Äther-Pyridin-Lösung bei Zimmertemperatur ein gelbes nadelförmiges Produkt vom Schmp. 188 ~189°C (II) (UV. λ_{Max}^{EtOH} $m\mu$ (ε): 262(24,300), 372(18,100)) von der Zusammensetzung $C_{30}H_{22}Cl_2$ (Ber. C, 79.47; H, 4.89; Cl, 15.64; Mol. Gew., 453.4. Gef. C, 79.04; H, 4.92; Cl, 15.62%; Mol. Gew. (Rast), 435) mit der Ausbeute von ca. 40 proz. der Theorie. In seinem IR-Spektrum ist ein C–H Band von der Acetylenbindung bei 3300 cm^{-1} verschwunden und bei 1950 cm^{-1} ist nur eine schwache Bande bemerkbar, die scheinbar nicht der Allenbindung, sondern dem substituierten Benzolring zu zuschreiben ist. Seine 2 Chloratome sind durch die Acetoxylgruppe ersetzbar, wenn man II in Eisessig-Lösung mit wasserfreiem Kaliumacetat unter Rückfluss erhitzt. Das entstandene Diacetat (III) ($C_{34}H_{28}O_4$-Ber. C, 81.57; H, 5.64; Mol. Gew. 500. Gef. C, 80.95; H, 5.70%; Mol. Gew., 494. UV. λ_{Max}^{EtOH} $m\mu$ (ε): 261(30,000), 363(20,000). IR. ν cm^{-1} (in Nujol): 1745 (Acetat)) bildet schwachgelbe Nadeln vom Schmp. 222°C und ergab beim Verseifen mit Salzsäure kein Produkt, das sich zu dem Brady'schen Reagens positiv verhält, sodaß die Enolacetat-Gruppe in ihm nicht vorhanden ist. Durch Ozon-Abbau von II konnte man ca. 1.6 Mol. Benzophenon erfassen und nebenbei eine chlorhaltige γ-Dicarbonsäure isolieren, die in das entsprechende Pyrrol übergeführt und durch die Ehrlich'sche Probe des letzteren bestätigt wurde. Diese Daten zeigen, daß II höchstwahrscheinlich einen Bisdiphenylmethylencyclobutan-Ring enthält.

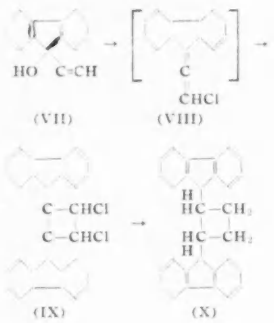
II widersteht der Reduktion mit $LiAlH_4$, man konnte es jedoch durch katalytische Reduktion mit Pd-Kohle in methanolischer Kali-Lösung in das entsprechende entchlorierte Tetrahydroderivat (IV) als farblose Nadeln vom Schmp. 153~154°C ($C_{30}H_{28}$-Ber. C, 92.73; H, 7.27. Gef. C, 92.57; H, 7.23%) überführen. Andererseits ergab II beim Erhitzen mit frisch bereitetem Raney-Nickel W-7 in Tetrahydrofuran-Lösung das entsprechende entchlorierte Produkt (V) ($C_{30}H_{24}$-Ber. C, 93.70; H, 6.30. Gef. C, 93.31; H, 6.48) als schwachgelbe Nadeln vom Schmp. 180~181°C (UV. λ_{Max}^{Dioxan} $m\mu$ (ε): 257(34,000), 352(28,000)), das mit der Beschreibung von 1,2-Bisdiphenylmethylencyclobutan[1] sehr ähnlich war. So wurde das letztere ausgehend von Adipinsäure über *trans*-Cyclobutandicarbonsäure[2] nach Alberman und Kipping[1] hergestellt und seine Identität mit V wurde durch eine Mischprobe sowie direkten Vergleich der IR-Spektren tatsächlich festgestellt. Die Konstitution von II ist dementsprechend 3,4-Dichlor-1,2-bisdiphenylmethylencyclobutan.

Die Entstehung von II aus I kann man nur in der Weise erklären, daß das zuerst durch eine anionotrope Umlagerung entstandene 1,1-Diphenyl-3-chlorallen (VI) dimerisiert hat. Zu bemerken ist dabei, daß in der Mutterlauge von II keine Allenverbindung IR-spektrographisch nachweisbar war.

1) K. B. Alberman und F. B. Kipping, *J. Chem. Soc.*, 1951, 776.
2) E. R. Buchman, A. O. Reims, T. Skei und M. J. Schlatter, *J. Am. Chem. Soc.*, **64**, 2696 (1942).



Es ist daher merkwürdig, daß Hennion und seine Forschungsgruppe[3] bei analoger Reaktion von 9-Äthinyl-9-fluorenol (VII) mit Thionylchlorid 9-Chlorvinylidenfluoren (VIII) erhielten. So wurde VII aufs neue nach der Beschreibung von Hennion et al. in wasserfreier Äther-Lösung bei Gegenwart von wasserfreiem Pyridin mit Thionylchlorid behandelt und gelbe Nadeln vom Schmp. 223～224°C (u. Zers.) IX in einer Ausbeute von 71.5 proz. erhalten, die mit der literarischen Angabe[3] gut übereinstimmten. Dasselbe Produkt wurde auch durch Einwirkung von konz. Salzsäure auf VII in einer Ausbeute von 74 proz. erhalten. Die Zusammensetzung von IX stimmte jedoch nicht mit VIII ($C_{15}H_9Cl$) sondern mit $C_{30}H_{18}Cl_2$ (Ber. C, 80.18; H, 4.03; Cl, 15.78; Mol. Gew., 449.4. Gef. C, 79.92; H, 4.25; Cl, 15.78%; Mol. Gew. (Rast) 428) überein. Ferner im Gegensatz zur literarischen Angabe wurde im IR-Spektrum von IX keine scharfe Bande einer Allenbindung bei 1950 cm^{-1} bemerkt, obwohl bei 2000～1650 cm^{-1} Banden von einem substituierten Benzolring vorhanden waren. Außerdem ist das UV-Spektrum von IX (UV. $\lambda_{Max}^{CHCl_3}$ $m\mu$ (ε): 276(54,000), 375(30,000)) mit demjenigen von II sehr ähnlich und durch Ozon-Abbau von IX konnte man neben ca. 1.4 Mol. Fluorenon eine γ-Dicarbonsäure isolieren, wie bei dem Abbau von II. Diese Daten zeigen, daß IX kein 9-Chlorvinylidenfluoren sondern 3,4-Dichlor-1,2-bisfluorenylidencyclobutan ist, und daß die Reaktion von VII mit Thionylchlorid ganz analog wie beim I verläuft. Zur weiteren



Bestätigung wurde IX mit Pd-Kohle katalytisch reduziert, wobei man kein 9-Äthylfluoren vom Schmp. 108°C, sondern ein halogenfreies Kristall vom Schmp. 167～168°C (X) ($C_{30}H_{24}$-Ber. C, 93.71; H, 6.29. Gef. C, 93.13; H, 6.06%.) unter 4 Mol. Wasserstoff-Aufnahme erhalten konnte.

Herrn Prof. Dr. E. Ochiai und Herrn Dr. T. Shimamoto für ihre freundliche Leitung dieser Arbeit und Herrn Dr. I. Iwai für den Literarischen Hinweis und die Diskussion danke ich verbindlichst.

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3) G. F. Hennion und B. R. Fleck, ebenda, **77**, 3253 (1955).
4) N. D. Zelinsky und M. W. Gawerdowskaja, *Ber.*, **61**, 1052 (1928).

Mechanism of the Recoil Phenomena in Hexamminecobalt(III) Chloride

By Nagao Ikeda, Kenji Yoshihara and Shigeru Yamagishi

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In the previous paper[1], we studied the heterogeneous extraction of recoil atoms in neutron-irradiated hexamminecobalt(III) nitrate target, and observed the anomalously high extraction yield with this compound. In the present paper, we studied the recoil effects in hexamminecobalt(III) chloride and found the following two interesting facts. 1) The recoil effects in hexamminecobalt(III) chloride involve more complicated processes than the simple replacement process. 2) A small percentage of the activity produced in the target is found in the form of chloropentamminecobalt(III) chloride as the result of recoil effect, and its radiochemical yield decreases on keeping it to stand even at room temperature; the rate determining step in this process is not diffusion, which has been usually considered to be responsible to the thermal annealing process of the recoil atom[2], but a chemical reaction.

Purified hexamminecobalt(III) chloride was subjected to neutron irradiation in the reactor, JRR-1 (neutron flux: 6×10^{11} n/cm^2/sec.) for 10 min., and was dissolved in water in about

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2) G. Harbottle and N. Sutin, "The Szilard-Chalmers Reaction in Solids" in "Advances in Inorganic Chemistry and Radiochemistry" Edited by H. J. Emelius and A. G. Sharpe, Academic Press, New York (1959).

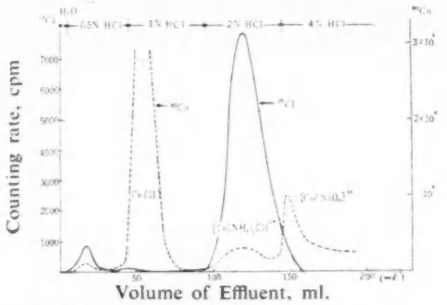

Fig. 1. Elution curve for recoil products in neutron-irradiated hexamminecobalt(III) chloride.

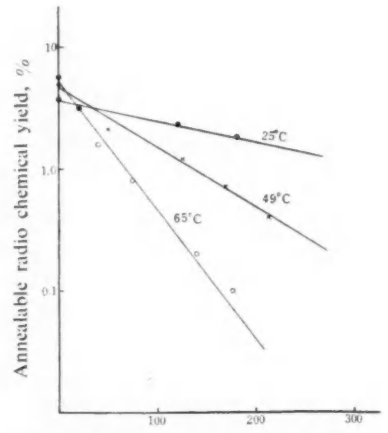

Fig. 2. Decrease of radiochemical yield of $[Co(NH_3)_5Cl^*]$ by standing irradiated hexamminecobalt(III) chloride at various temperatures.

30 min. after irradiation. The solution was passed through a cation-exchange resin column (Diaion SK #1, HR-form, 100~200 mesh, 1 cm. $\phi \times 4$ cm.). After being washed with a small quantity of water, the resin bed was eluted with hydrochloric acid of various concentrations. By the use of a pulse-height analyzoer, the γ-rays of ^{38}Cl and ^{60}Co in the eluted fractions were measured separately. The elution curve is shown in Fig. 1. The solid line shows the elution curve for ^{38}Cl activity and the dotted one shows that for ^{60}Co activity. The formation of $[Co(NH_3)_5Cl^*]^{2+}$ might be interpreted as simple replacement of NH_3 by ^{38}Cl recoil atom, but the formation of $[Co^*(NH_3)_5Cl]^{2+}$ can not be understood by this concept. Moreover, such a simple replacement can not explain the appearance of a peak at the earlier stage of the elution curve; a peak due to an unknown species containing both cobalt and chlorine atoms which might be a cobalt ammine complex, such as $[Co(NH_3)_4Cl_2]^+$.

The radiochemical yield of $[Co(NH_3)_5Cl^*]^{2+}$ was accurately measured after being separated from the luteo-salt. It was about 7% immediately after irradiation, but this value decreased on keeping the sample to stand in the solid state. At various temperatures, the relation between the standing time and the radiochemical yield of $[Co(NH_3)_5Cl^*]^{2+}$ was observed. The annealing curves for the earlier stage are shown in Fig. 2. The curves correspond to those of the first-order reaction. An apparent activation energy of 8.6 kcal. was obtained for this decreasing process of $[Co(NH_3)_5Cl^*] \cdot Cl_2$. Mori and Tsuchiya[3] studied the thermal decomposition of $[Co(NH_3)_6]Cl_3$ and reported the heat of formation $\Delta H = 9.6$ kcal./mol. and the activation energy $E_b = 18.0$ kcal./mol. for the reaction,

$$[Co(NH_3)_6]Cl_3 \rightleftarrows [Co(NH_3)_5Cl]Cl_2 + NH_3$$
(solid) (solid) (gas)

In the back-reaction, therefore, the activation energy $E_p = E_b - \Delta H = 8.4$ kcal./mol. is obtained. This value is very close to that obtained in this experiment. So that, one possible explanation of the annealing reaction observed by the present authors may be given by considering the back-reaction of the above-mentioned system provided that the quantity of ammonia is much larger compared with that of $[Co(NH_3)_5Cl]Cl_2$.

These results would lead us to the following model. In the neighborhood of the recoil atom, the chemical bonds of the molecules are broken and local fragmentation occurs. Unstable intermediate systems are formed. These are immediately rearranged into a group of several chemical species in the cooling step. However, some unbalances are still present in these systems, and slow changes occur by thermal annealing.

Details are to be reported in the full paper.

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Nuclear Quadrupole Resonance of B-Trichloroborazole

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In an attempt to obtain some informations on the electronic structure of borazole and its derivatives, the pure quadrupole resonance of ^{35}Cl in solid *B*-trichloroborazole was observed using a spectrometer previously reported[1]. The compound was synthesized by Brown and Laubengayer's method[2] and purified by sublimation immediately before measurements. The observed frequency was 19.937 and 19.639± 0.001 Mc. at liquid nitrogen temperature and room temperature (22.0°C), respectively. The signal-to-noise ratio was about 3 as observed on an oscilloscope display. The compound underwent gradual decomposition, a sample left to stand in a sealed glass tube for a month showing no observable resonance line on the oscilloscope screen. A search for the resonance lines of *B*-trichloro-*N*-trimethylborazole and *B*-trichloro-*N*-triphenylborazole was unsuccessful, presumably because the lines were broadened to escape detection.

The X-ray crystal analysis carried out on *B*-trichloroborazole by Coursen and Hoard[3] has shown that all the chlorine atoms are equivalent in the crystal lattice. This is in agreement with the observation of a single resonance line in the present study.

The B-Cl distance 1.75 Å in this molecule determined by both X-ray crystal analysis and electron diffraction investigation[4] is practically identical with that in a boron trichloride molecule[5]. In addition, chlorine and nitrogen have the same value of electronegativity equal to 3.0 as proposed by Pauling[6]. This suggests a striking similarity existing between the atomic environments about chlorine atoms in these two compounds. Accordingly, one may expect the same p-electron defect[7] on these chlorine atoms leading to nearly the same frequency of the quadrupole resonance. As a matter of fact, the observed frequency of ^{35}Cl in solid boron trichloride at liquid nitrogen temperature, 21.6 Mc.[8,9] is fairly close to that in *B*-trichloroborazole, 19.9 Mc., of the present study. The reason for the difference must be looked for in the partial aromatic character of a borazole ring[10], in which π-electrons are presumed to migrate to some extent from nitrogen to boron[11]. As a result of Kekulé type resonance, the ionic character of B-Cl bonds will increase. Accordingly, the p-electron defect on chlorine atoms decreases, leading to the decrease in the frequency of quadrupole resonance as observed in the present investigation. A quantitative treatment must be postponed until the asymmetry parameter of field gradient is determined and complications involved in the partial ionic character and double bond character* of the B-Cl bond are clarified in future.

Mention shuld be made here of studies on the ^{35}Cl pure quadrupole resonances of some heterocyclic compounds made by Negita and coworkers[12], who showed that the observed resonance frequencies of $(-SCl=N-)_3$, $(-PCl_2=N-)_3$ and $(-CCl=N-)_3$ were fairly close to those of $SOCl_2$, $POCl_3$ and $COCl_2$, respectively. The partial molecular structure of these heterocyclic compounds is more or less analogous to that of the corresponding oxychlorides as in the pair of compounds, *B*-trichloroborazole $(-BCl=NH-)_3$ and boron trichloride BCl_3.

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* The double bond character of B-Cl bonds was estimated at only 6% in boron trichloride[9].
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